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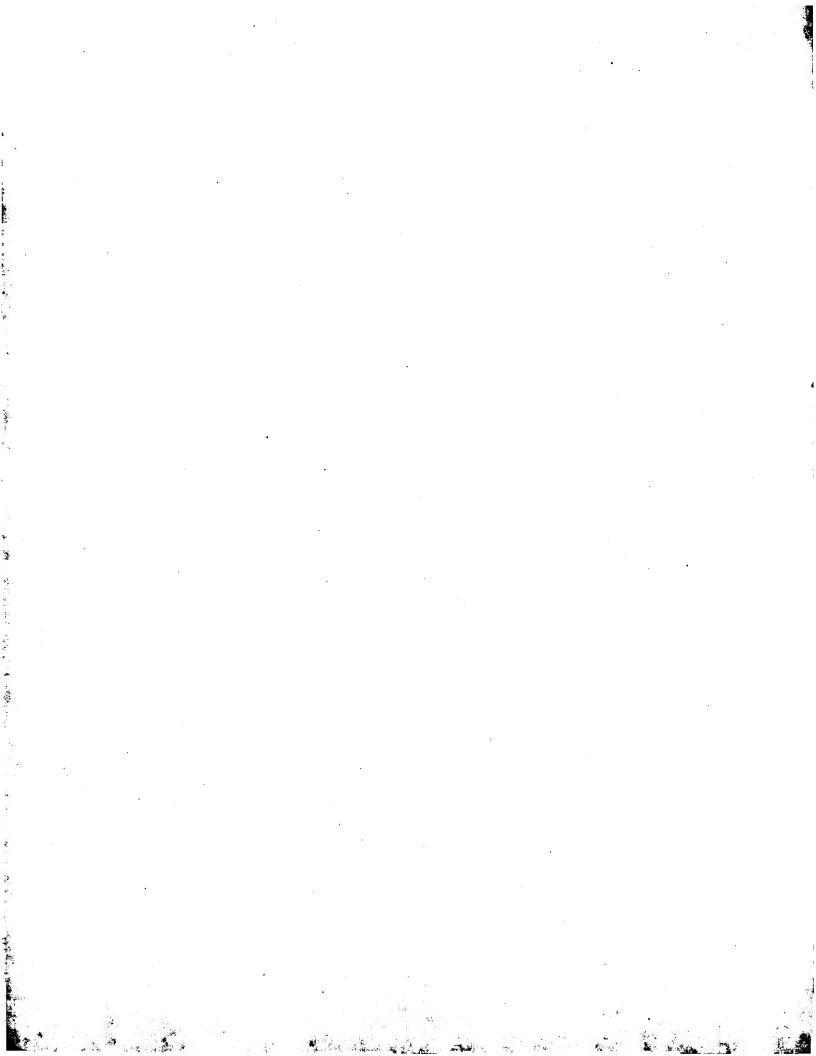
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(54) Title: FOOD CLEANING COMPOSITIONS CONTAINING CYCLODEXTRIN

(57) Abstract

The presente invention relates to a stable, preferably aqueous, food cleaning composition, preferably for use on produce and/or food contact surfaces. The composition typically comprises from about 0.1 % to about 20 %, by weight of the composition, of solubilized, water-soluble, uncomplexed cyclodextrin and an effective amount of at least one ingredient to improve the performance of the composition selected from the group consisting of: (1) cyclodextrin compatible surfactant; (2) cyclodextrin compatible antimicrobial active; and (3) mixtures thereof. Optional hydrophilic perfume improves acceptance. Optionally, the composition can contain low molecular weight polyols; metallic salts to help control odor, etc. The composition is preferably essentially free of any material that is not food compatible. The composition is preferably applied as small particle size droplets, especially from spray containers. The surfactant/antibacterial active combination, provides improved antimicrobial activity.

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FOOD CLEANING COMPOSITIONS CONTAINING CYCLODEXTRIN

TECHNICAL FIELD

The present invention relates to stable, preferably clear, aqueous food cleaning compositions, articles of manufacture, and/or method of use, comprising: solubilized, uncomplexed cyclodextrin; cyclodextrin compatible surfactant; optionally, cyclodextrin compatible antimicrobial active, optionally, hydrophilic perfume providing improved acceptance; or mixtures thereof. As used herein, "cyclodextrin compatible" means that the cyclodextrin and the other material, or active, do not substantially interact so as to eliminate the ability of cyclodextrin to absorb odor and other undesirable organic molecules, or the desired effect of the material or active. The food cleaning composition is designed to remove and/or eliminate undesirable materials, such as soil, organic residue materials such as pesticides, odors caused by a broad spectrum of organic odoriferous materials, on food products and/or food contacting surfaces, such as produce, fruits and vegetables, meat, poultry, fish and other seafoods, food preparing surfaces and/or equipment, such as cutting board, countertop, pots and pans, food containers, and the like. The food cleaning composition preferably remain shelf stable for a substantial period of time.

BACKGROUND OF THE INVENTION

It is well-known and appreciated by consumers that fruits and vegetables should be thoroughly washed prior to ingestion in order to remove soils and other unwanted residues which may be undesirably clinging to the surfaces thereof. Besides dirt, there can be other types of unwanted residues such as chemical residues and biological residues. Examples of chemical residues are pesticides, herbicides, fungicides, sprouting inhibitors and fertilizers. Examples of biological residues are microorganisms that can be pathogenic. Many of the chemical residues have very low solubility in water and some are practically insoluble in water. Typical examples of such chemical residues (with function and crops they are applied to) are Azinphosmethyl (insecticide for apples, peaches), Benomyl (fungicide for apples, peaches, tomatoes, cucumbers, broccoli, beans), Captan (fungicide for apples, peaches, cucumbers), Chorothalonil (fungicide for tomatoes, carrots, beans, cucumbers, broccoli) Chlorpropham (sprouting inhibitor for potatoes), Dicloran (fungicide for peaches), diphenyl amine (screw worm repellant and post harvest fungicide for apples), Folpet (fungicide for tomatoes), Iprodione (fungicide for peaches, grapes), Linuron (herbicide for carrots), Permethrin (insecticide for lettuce), thiabendazole (fungicide and nematocide for bananas, potatoes, apples) and Vinclozolin (fungicide for grapes, strawberries). It has been estimated that about 95% of consumers recognize the need for thorough washing but, ordinarily, only use tap water for this purpose. On the order of about 5% of those consumers who do wash their vegetables use a household cleaner, typically a liquid dishwashing product. However, dishwashing products are not specifically intended for such use, inasmuch as they are usually designed to provide high, persistent suds which makes them inconvenient to remove from the fruits or vegetables which have been washed therewith.

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Uncooked food such as meat, poultry, fish and other seafoods can have particular odor, especially when they are stored and/or frozen for some time and are not fresh. Other food, especially condiments such as garlic, onion, curry, can leave a noticeable and undesirable odor on food preparing surfaces such as cutting boards and wooden spoons, which are very difficult to remove. It is also common to have soils and other unwanted residues undesirably clinging on other food preparation or contact surfaces in consumer's homes on surfaces such as kitchen counters, sinks, cuttery, etc., as well as food preparation or contact surfaces which also include processing bins, cooking trays, etc., in commercial and/or industrial facilities such as restaurants, cafeterias, supermarkets, and the like.

It is desirable to have a food cleaning composition that is effective in removing these unwanted residues from food and food contacting surfaces. Liquid solutions are convenient for the user, since they can be applied directly to soiled fruits, vegetables, and other food and food contacting surfaces, followed by rinsing in tap water.

The present invention relates to stable, preferably clear, aqueous food cleaning and odor absorbing compositions, articles of manufacture and/or method for use. The clarity of the liquids connotes cleanliness to the user and is thus highly desirable. Preferably, the compositions are sprayed onto food products and surfaces, with optional scrubbing, and rinsed off, to remove unwanted residues and/or to restore their freshness by reducing the unwanted off-odor.

Low sudsing is an important attribute so that removal of the solution by rinsing is achieved quickly and easily. It is also advantageous if such compositions are provided in the form of concentrates, which can be diluted by the consumer before use and/or applied to the fruits, vegetables and other food as a direct spray-on.

Uncomplexed cyclodextrin molecules, which are made up of varying numbers of glucose units can absorb many organic materials, such as the chemical residues and off-odor molecules listed hereinabove to improve their removability. While cyclodextrin is an effective absorbing active for organic molecules, some small

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molecules are not sufficiently absorbed by the cyclodextrin molecules because the cavity of the cyclodextrin molecule may be too large to adequately hold the smaller organic molecule. If a small sized organic odor molecule is not sufficiently absorbed into the cyclodextrin cavity, a substantial amount of malodor can remain. In order to alleviate this problem, low molecular weight polyols can be added to the composition to enhance the formation of cyclodextrin inclusion complexes. Furthermore, optional water soluble metal salts can be added to complex with some nitrogen-containing and sulfur-containing malodor molecules.

It is also desirable that the compositions contain a cyclodextrin compatible and food approved surfactant to provide the cleaning performance and to improve the removal of dirt and other undesirable materials.

Such compositions can optionally provide a "scent signal" in the form of a pleasant odor, such as a fruity odor, which signals the removal of the malodor and/or other undesirable materials.

It is desirable to provide further improvements such as a cyclodextrin compatible and food compatible antimicrobial active that provides substantial reduction of microorganisms that cause, e.g., odor, infections, etc., which exist on food and/or food preparation surfaces. It is more preferable that the food cleaning compositions of the present invention contain both a antibacterial active and a surfactant, with both being cyclodextrin compatible and food compatible.

Since cyclodextrin can be an organic nutrient for certain microorganisms, especially when in aqueous compositions, it is preferable to include a water-soluble and food compatible antimicrobial preservative, which is effective for inhibiting and/or regulating microbial growth, to increase storage stability of clear, aqueous food cleaning and odor-absorbing solutions containing water-soluble cyclodextrin, when the composition does not contain an antimicrobial material as described hereinbelow.

A cyclodextrin-compatible active is one which does not substantially form a complex with cyclodextrin in the composition, at the usage concentration, so that an effective amount of both the free, uncomplexed active and free, uncomplexed cyclodextrin are available for their intended use.

It is desirable for the materials incorporated in the food cleaning compositions of the present invention to be food compatible, e.g., suitable for direct or indirect food contact use and/or may be approved as GRAS, prior sanctioned, or subject to GRAS approval via a GRAS petition, for example, a new chemical developed for this invention, and/or toxicologically acceptable to humans under usage conditions. Materials added to foods (additives) may be categorized as one of several types: (1)

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direct food additives; (2) indirect food additives; (3) GRAS ingredients (generally recognized as safe) either as direct or indirect food substances; (4) GRAS affirmed, a chemical which may be considered for GRAS classification after experts review adequate technical support data for the GRAS petition; and (5) prior sanctioned, a food ingredient of known food use and granted approval with respect to use of the substance in food prior to September 1958, by the FDA, or USDA.

Food additives include substances the intended use of which results or may reasonably be expected to result, directly or indirectly, either in their becoming a component of food or otherwise affecting the characteristics of food. As an example, a material used in the production of food containers and/or packaging materials is subject to the definition if it may become an ingredient in the food, or to affect the characteristics, directly or indirectly, of the food in the container or package. In net, direct food additive are those materials which are added directly to foods to achieve a desirable or intended purpose.

Indirect food additives are those which are added to food containers and/or packages, and which may result in the food simply because of contact of the container/package with the food. Indirect food additives may include: (1) adhesives and components of coatings; (2) paper and paperboard components; (3) adjuvants, such as those used in the manufacture of foamed plastics, and sanitizers. Sanitizers used in food applications, as direct or indirect, are many and may consists of, but are not limited to: (1) aqueous hypochlorite (K, Na or Ca salts); (2) aqueous solution of dichloroisocyanuric acid, trichloroisocyanuric acid, or the sodium or potassium salts of these acids, with or without the bromides of potassium, sodium, or calcium; (3) anionic surfactant solutions such as dodecylbenzene sulfonic acid, and/or sodium lauryl sulfate; or mixtures of these together or with other anionic surfactants as allowed under FDA regulations; (4) aqueous fatty acid solutions containing decanoic acid, octanoic acid, lactic acid and other ingredients; (5) aqueous solutions comprised of hydrogen peroxide, peroxyacetic acid, acetic acid, sulfuric acid and other ingredients as allowed by FDA regulations: (6) quaternary sanitizers such as di-nalkyl (C₈₋₁₀) dimethylammonium chloride components, n-alkyl (C₁₂₋₁₆) benzyldimethylammonium chloride components along with other quaternary actives; (7) aqueous solutions containing ortho-phenylphenol, ortho-benzyl-para-chlorophenol, para-tertiaryamylphenol and other ingredients as allowed under FDA regulations.

Substances added directly to human food may be affirmed as generally recognized as safe (GRAS). Direct GRAS ingredients shall be used under current good manufacturing practice which includes that a direct human food ingredient be of appropriate food grade; that it be prepared and handled as a food ingredient, and that

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the quantity of the ingredient added to food does not exceed the amount reasonably required to accomplish the intended physical, nutritional, or other technical effect in the food item.

Indirect GRAS ingredients are those which may be used in the container, packaging and/or wrapper, and which may migrate into the food items because of their close proximity to the food. Indirect GRAS ingredients shall be used under current good manufacturing practice which includes that an indirect human food ingredient be of appropriate purity; and that the quantity of the ingredient added to food container, packaging, wrapper, etc. does not exceed the amount reasonably required to accomplish the intended physical, nutritional, or other technical effect in the food-contact item.

SUMMARY OF THE INVENTION

The present invention relates to a stable, preferably clear, preferably aqueous, food cleaning composition, preferably for use on food and food contacting surfaces, such as food preparing equipment and/or food containers, comprising:

- (A). an effective amount to remove organic residue materials and/or absorb malodors, typically from about 0.01% to about 20% by weight of the composition, with concentrated compositions which are meant to be diluted containing from about 3% to about 20%, preferably from about 5% to about 10% by weight of the composition, and, for more dilute "usage conditions" compositions, a range of from about 0.01% to about 5%, preferably from about 0.1% to about 3%, more preferably from about 0.5% to about 2%, by weight of the usage composition, of solubilized, uncomplexed cyclodextrin;
- (B). optionally, an effective amount to remove soil and/or improve the performance of the composition, typically from about 0.01% to about 5%, preferably from about 0.03% to about 3%, and more preferably from about 0.05% to about 2%, by weight of the usage composition, of cyclodextrin compatible surfactant that preferably provides a surface tension of from about 20 dyne/cm to about 60 dyne/cm, preferably from about 20 dyne/cm to about 45 dyne/cm (with concentrated compositions having a level of from about 0.1% to about 15%, preferably from about 0.2% to about 10%, more preferably from about 0.3% to about 3%, by weight of the concentrated solution, of cyclodextrin-compatible surfactant);
- (C). optionally, an effective amount, to kill, or reduce the growth of microbes, of cyclodextrin compatible and water soluble antimicrobial

active, preferably from about 0.001% to about 0.8%, more preferably from about 0.002% to about 0.3%, even more preferably from about 0.003% to about 0.2%, by weight of the usage composition (with concentrated compositions having a level of from about 0.003% to about 2%, preferably from about 0.01% to about 1.2%, more preferably from about 0.1% to about 0.8%, by weight of the concentrated solution, of cyclodextrin-compatible and water soluble antimicrobial active);

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(D). optionally, an effective amount of sequestrant/builder to improve cleaning, preferably from about 0.0005% to about 3%, more preferably from about 0.005% to about 0.5%, and even more preferably from about 0.01% to about 0.2%, by weight of the usage composition;

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optionally, but preferably, an effective amount to improve acceptance **(E)**. of the composition, typically from about 0.003% to about 0.5%, preferably from about 0.01% to about 0.3%, more preferably from about 0.05% to about 0.2%, by weight of the usage composition of hydrophilic perfume, containing at least about 50%, preferably at least about 60%, more preferably at least about 60%, even more preferably at least about 70%, and yet more preferably at least about 80%, by weight of the perfume of perfume ingredients that have a ClogP of less than about 3.5 and optionally, a minor amount of perfume ingredients selected from the group consisting of ambrox, bacdanol, benzyl salicylate, butyl anthranilate, cetalox, damascenone, alphadamascone, gamma-dodecalactone, ebanol, herbavert, cis-3-hexenyl salicylate, alpha-ionone, beta-ionone, alpha-isomethylionone, lilial, methyl nonyl ketone, gamma-undecalactone, undecylenic aldehyde, and mixtures thereof;

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- (F). optionally, but preferably, from about 0.01% to about 3%, more preferably from about 0.05% to about 1%, and even more preferably from about 0.1% to about 0.5%, by weight of the usage composition of low molecular weight polyol;
- (G). optionally, from about 0.001% to about 0.3%, preferably from about 0.01% to about 0.1%, more preferably from about 0.02% to about 0.05%, by weight of the usage composition of chelator, e.g., aminocarboxylate chelator,

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(H). optionally, from about 0.01% to about 2%, preferably from about 0.05% to about 1%, more preferably from about 0.1% to about 0.5%, by weight of the usage composition of antifoaming agent;

(I). optionally, but preferably, an effective of metallic salt, preferably from about 0.1% to about 10%, more preferably from about 0.2% to about 8%, even more preferably from about 0.3% to about 5%, by weight of the usage composition, especially water soluble zinc salts, for improved odor benefit;

(J). optionally, an effective amount of enzyme, from about 0.0001% to about 0.5%, preferably from about 0.001% to about 0.3%, more preferably from about 0.005% to about 0.2% by weight of the usage composition, for improved cleaning and/or odor control benefit;

(K). optionally, an effective amount of solubilized, water-soluble, antimicrobial preservative, preferably from about 0.0001% to about 0.5%, more preferably from about 0.0002% to about 0.2%, most preferably from about 0.0003% to about 0.1%, by weight of the composition;

(L). optionally, an effective amount of adjunct odor-controlling ingredients, preferably selected from the group consisting of alkali carbonate and bicarbonate salts, low molecular weight water soluble ionic polymers, and mixtures thereof; and preferably present at a level of from about 0.005% to about 5%, more preferably from about 0.01% to about 3%, and even more preferably from about 0.1% to about 2%, by weight of the usage composition; and

(M). aqueous carrier, said composition containing at least one of (B) and (C), and preferably containing only ingredients which are food compatible.

The present invention also relates to concentrated compositions, wherein the level of cyclodextrin is from about 3% to about 20%, more preferably from about 5% to about 10%, by weight of the composition which are diluted to form compositions with the usage concentrations of cyclodextrin of, e.g., from about 0.1% to about 5%, by weight of the diluted composition, as given hereinabove, which are to the "usage conditions".

The present invention also relates to the food cleaning compositions incorporated into a spray dispenser to create an article of manufacture that can facilitate treatment of food surfaces with said compositions containing uncomplexed cyclodextrin and other optional ingredients at a level that is effective. Said

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compositions and/or article of manufacture are preferably in association with instructions to use said compositions and product at an effective level to remove undesirable materials from food and/or food preparation surfaces.

The present invention also relates to methods of using said food cleaning composition, either alone, or incorporated into a spray dispenser, to remove and/or eliminate undesirable materials, such as soil, pesticides, odors caused by a broad spectrum of organic odoriferous materials, from food products, such as produce, fruits and vegetables, meat, poultry, fish and other seafoods, and/or food preparing surfaces, such as cutting board, countertop, pots and pans, food containers, and the like.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a stable, preferably clear, aqueous food cleaning composition, preferably for use on food and food contacting surfaces, such as food preparing equipment and/or food containers, comprising:

- (A). an effective amount to remove organic residue materials and/or absorb malodors, typically from about 0.01% to about 20% by weight of the composition, with concentrated compositions which are meant to be diluted containing from about 3% to about 20%, preferably from about 5% to about 10% by weight of the composition, and, for more dilute "usage conditions" compositions, a range of from about 0.01% to about 5%, preferably from about 0.1% to about 3%, more preferably from about 0.5% to about 2%, by weight of the usage composition, of solubilized, uncomplexed cyclodextrin;
- (B). optionally, an effective amount to remove soil and/or improve the performance of the composition, typically from about 0.01% to about 5%, preferably from about 0.03% to about 3%, and more preferably from about 0.05% to about 2%, by weight of the usage composition, of cyclodextrin compatible surfactant that preferably provides a surface tension of from about 20 dyne/cm to about 60 dyne/cm, preferably from about 20 dyne/cm to about 45 dyne/cm (with concentrated compositions having a level of from about 0.1% to about 15%, preferably from about 0.2% to about 10%, more preferably from about 0.3% to about 3%, by weight of the concentrated solution, of cyclodextrin-compatible surfactant);
- (C). optionally, an effective amount, to kill, or reduce the growth of microbes, of cyclodextrin compatible and water soluble antimicrobial active, preferably from about 0.001% to about 0.8%, more preferably

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(E).

from about 0.002% to about 0.3%, even more preferably from about 0.003% to about 0.2%, by weight of the usage composition (with concentrated compositions having a level of from about 0.003% to about 2%, preferably from about 0.01% to about 1.2%, more preferably from about 0.1% to about 0.8%, by weight of the concentrated solution, of cyclodextrin-compatible and water soluble antimicrobial active);

(D). optionally, an effective amount of sequestrant/builder to improve cleaning, preferably from about 0.0005% to about 3%, more preferably from about 0.005% to about 0.5%, and even more preferably from about 0.01% to about 0.2%, by weight of the usage composition;

optionally, but preferably, an effective amount to improve acceptance of the composition, typically from about 0.003% to about 0.5%, preferably from about 0.01% to about 0.3%, more preferably from about 0.05% to about 0.2%, by weight of the usage composition of hydrophilic perfume, containing at least about 50%, preferably at least about 60%, more preferably at least about 60%, even more preferably at least about 70%, and yet more preferably at least about 80%, by weight of the perfume of perfume ingredients that have a ClogP of less than about 3.5 and optionally, a minor amount of perfume ingredients selected from the group consisting of ambrox, bacdanol, benzyl salicylate, butyl anthranilate, cetalox, damascenone, alphadamascone, gamma-dodecalactone, ebanol, herbavert, cis-3-hexenyl salicylate, alpha-ionone, beta-ionone, alpha-isomethylionone, lilial, methyl nonyl ketone, gamma-undecalactone, undecylenic aldehyde, and mixtures thereof;

(F). optionally, but preferably, from about 0.01% to about 3%, more preferably from about 0.05% to about 1%, and even more preferably from about 0.1% to about 0.5%, by weight of the usage composition of low molecular weight polyol;

(G). optionally, from about 0.001% to about 0.3%, preferably from about 0.01% to about 0.1%, more preferably from about 0.02% to about 0.05%, by weight of the usage composition of chelator, e.g., aminocarboxylate chelator;

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- (H). optionally, from about 0.01% to about 2%, preferably from about 0.05% to about 1%, more preferably from about 0.1% to about 0.5%, by weight of the usage composition of antifoaming agent;
- (I). optionally, but preferably, an effective of metallic salt, preferably from about 0.1% to about 10%, more preferably from about 0.2% to about 8%, even more preferably from about 0.3% to about 5%, by weight of the usage composition, especially water soluble zinc salts, for improved odor benefit;
- (J). optionally, an effective amount of enzyme, from about 0.0001% to about 0.5%, preferably from about 0.001% to about 0.3%, more preferably from about 0.005% to about 0.2% by weight of the usage composition, for improved cleaning and/or odor control benefit;
- (K). optionally, an effective amount of solubilized, water-soluble, antimicrobial preservative, preferably from about 0.0001% to about 0.5%, more preferably from about 0.0002% to about 0.2%, most preferably from about 0.0003% to about 0.1%, by weight of the composition;
- (L). optionally, an effective amount of adjunct odor-controlling ingredients, preferably selected from the group consisting of alkali carbonate and bicarbonate salts, low molecular weight water soluble ionic polymers, and mixtures thereof; and preferably present at a level of from about 0.005% to about 5%, more preferably from about 0.01% to about 3%, and even more preferably from about 0.1% to about 2%, by weight of the usage composition; and
- (M). aqueous carrier, said composition containing at least one of (B) and (C), and containing, essentially, only ingredients which are food compatible, and/or preferably having a pH of more than about 3, more preferably more than about 3.5, said composition optionally being packaged in a container that is capable of dispensing said composition as either 1) small droplets having a weight average diameter of from about 10 μm to about 120 μm. and/or 2) a foam, said container optionally being part of an article of manufacture which also comprises non-manually operated spray means, and/or said composition being packaged in association with instructions to use it to clean and/or deodorize food and/or food contact surfaces.
- The present invention also relates to concentrated compositions, wherein the level of cyclodextrin is from about 3% to about 20%, preferably from about 4% to about 15%, more preferably from about 5% to about 10%, by weight of the

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concentrated composition. The concentrated composition is typically diluted to form usage compositions, with the usage concentration of, e.g., from about 0.1% to about 5%, by weight of the usage composition, as given hereinabove. Specific levels of other optional ingredients in the concentrated composition can readily be determined from the desired usage composition and the desired degree of concentration.

I. COMPOSITION

(A). CYCLODEXTRIN

As used herein, the term "cyclodextrin" includes any of the known cyclodextrins such as unsubstituted cyclodextrins containing from six to twelve glucose units, especially, alpha-cyclodextrin, beta-cyclodextrin, gamma-cyclodextrin and/or their derivatives and/or mixtures thereof. The alpha-cyclodextrin consists of six glucose units, the beta-cyclodextrin consists of seven glucose units, and the gamma-cyclodextrin consists of eight glucose units arranged in donut-shaped rings. The specific coupling and conformation of the glucose units give the cyclodextrins a rigid, conical molecular structures with hollow interiors of specific volumes. The "lining" of each internal cavity is formed by hydrogen atoms and glycosidic bridging oxygen atoms; therefore, this surface is fairly hydrophobic. The unique shape and physical-chemical properties of the cavity enable the cyclodextrin molecules to absorb (form inclusion complexes with) organic molecules or parts of organic molecules which can fit into the cavity. Many of the undesirable materials present of food products and odorous molecules can fit into the cavity. Therefore, cyclodextrins, and especially mixtures of cyclodextrins with different size cavities, can be used to improve removal of such undesirable materials and odors by forming more water soluble complexes. The undesirable odorous materials can be degradation products of food, caused by oxidation and/or bacterial degradation, or the residual odor of the food itself, such as condiments and spices, that remains and lingers on food preparing The complexation between cyclodextrin and organic materials occurs rapidly in the presence of water. However, the extent of the complex formation also depends on the polarity of the absorbed molecules. In an aqueous solution, strongly hydrophilic molecules (those which are highly water-soluble) are only partially absorbed, if at all. However, these materials are water soluble and are readily removable by the rinsing step.

The cavities within the cyclodextrin in the solution of the present invention should remain essentially unfilled (the cyclodextrin remains uncomplexed) while in solution, in order to allow the cyclodextrin to absorb various undesirable organic molecules when the solution is applied to a food surface. Non-derivatised (normal) beta-cyclodextrin can be present at a level up to its solubility limit of about 1.85%

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(about 1.85g in 100 grams of water) at room temperature. Beta-cyclodextrin is a GRAS affirmed material, and is preferred in the compositions of the present invention. Beta-cyclodextrin is not preferred in compositions which call for a level of cyclodextrin higher than its water solubility limit.

Preferably, the food cleaning composition of the present invention is clear. The term "clear" as defined herein means transparent or translucent, preferably transparent, as in "water clear," when observed through a layer having a thickness of less than about 10 cm.

Preferably, the cyclodextrins used in the present invention are highly watersoluble such as, alpha-cyclodextrin and/or derivatives thereof, gamma-cyclodextrin and/or derivatives thereof, derivatised beta-cyclodextrins, and/or mixtures thereof. The derivatives of cyclodextrin consist mainly of molecules wherein some of the OH groups are converted to OR groups. Cyclodextrin derivatives include, e.g., those with short chain alkyl groups such as methylated cyclodextrins, and ethylated cyclodextrins, wherein R is a methyl or an ethyl group; those with hydroxyalkyl substituted groups, such as hydroxypropyl cyclodextrins and/or hydroxyethyl cyclodextrins, wherein R is a -CH2-CH(OH)-CH3 or a -CH2-CH2-OH group; branched cyclodextrins such as maltose-bonded cyclodextrins; cationic cyclodextrins such as those containing 2-hydroxy-3-(dimethylamino) propyl ether, wherein R is CH2-CH(OH)-CH2-N(CH3)2 which is cationic at low pH; quaternary ammonium, e.g., 2-hydroxy-3-(trimethylammonio)propyl ether chloride groups, wherein R is CH2-CH(OH)-CH2-N⁺(CH3)3Cl⁻; anionic cyclodextrins such as carboxymethyl cyclodextrins, cyclodextrin sulfates, and cyclodextrin succinylates; amphoteric as carboxymethyl/quaternary ammonium cyclodextrins; cyclodextrins such cyclodextrins wherein at least one glucopyranose unit has a 3-6-anhydro-cyclomalto structure, e.g., the mono-3-6-anhydrocyclodextrins, as disclosed in "Optimal Performances with Minimal Chemical Modification of Cyclodextrins", F. Diedaini-Pilard and B. Perly, The 7th International Cyclodextrin Symposium Abstracts, April 1994, p. 49, said references being incorporated herein by reference; and mixtures thereof. Other cyclodextrin derivatives are disclosed in U.S. Pat. Nos: 3,426,011, Parmerter et al., issued Feb. 4, 1969; 3,453,257; 3,453,258; 3,453,259; and 3,453,260, all in the names of Parmerter et al., and all issued July 1, 1969; 3,459,731, Gramera et al., issued Aug. 5, 1969; 3,553,191, Parmerter et al., issued Jan. 5, 1971; 3,565,887, Parmerter et al., issued Feb. 23, 1971; 4,535,152, Szejtli et al., issued Aug. 13, 1985; 4,616,008, Hirai et al., issued Oct. 7, 1986; 4,678,598, Ogino et al., issued Jul. 7, 1987; 4,638,058, Brandt et al., issued Jan. 20, 1987; and 4,746,734,

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Tsuchiyama et al., issued May 24, 1988; all of said patents being incorporated herein by reference.

Highly water-soluble cyclodextrins are those having water solubility of at least about 10 g in 100 ml of water at room temperature, preferably at least about 20 g in 100 ml of water, more preferably at least about 25 g in 100 ml of water at room temperature. The availability of solubilized, uncomplexed cyclodextrins is essential for effective and efficient odor control performance. Solubilized, water-soluble cyclodextrin can exhibit more efficient removal of undesirable materials.

Examples of preferred water-soluble cyclodextrin derivatives suitable for use herein are hydroxypropyl alpha-cyclodextrin, methylated alpha-cyclodextrin, methylated beta-cyclodextrin, hydroxyethyl beta-cyclodextrin, and hydroxypropyl beta-cyclodextrin. Hydroxyalkyl cyclodextrin derivatives preferably have a degree of substitution of from about 1 to about 14, more preferably from about 1.5 to about 7, wherein the total number of OR groups per cyclodextrin is defined as the degree of Methylated cyclodextrin derivatives typically have a degree of substitution. substitution of from about 1 to about 18, preferably from about 3 to about 16. A known methylated beta-cyclodextrin is heptakis-2,6-di-O-methyl-\u00a3-cyclodextrin, commonly known as DIMEB, in which each glucose unit has about 2 methyl groups with a degree of substitution of about 14. A preferred, more commercially available, methylated beta-cyclodextrin is a randomly methylated beta-cyclodextrin, commonly known as RAMEB, having different degrees of substitution, normally of about 12.6. RAMEB is more preferred than DIMEB, since DIMEB affects the surface activity of the preferred surfactants more than RAMEB. The preferred cyclodextrins are available, e.g., from Cerestar USA, Inc. and Wacker Chemicals (USA), Inc.

It is also preferable to use a mixture of cyclodextrins. Such mixtures absorb odors more broadly by complexing with a wider range of odoriferous molecules having a wider range of molecular sizes. Preferably at least a portion of the cyclodextrins is alpha-cyclodextrin and its derivatives thereof, gamma-cyclodextrin and its derivatives thereof, and/or derivatised beta-cyclodextrin, more preferably a mixture of alpha-cyclodextrin, or an alpha-cyclodextrin derivative, and derivatised beta-cyclodextrin, even more preferably a mixture of derivatised alpha-cyclodextrin and derivatised beta-cyclodextrin, most preferably a mixture of hydroxypropyl alpha-cyclodextrin and hydroxypropyl beta-cyclodextrin, and/or a mixture of methylated alpha-cyclodextrin and methylated beta-cyclodextrin.

For more complete coverage of the surfaces being treated, the composition is preferably used as a spray. It is preferable that the usage compositions of the present invention contain low levels of cyclodextrin for efficiency and removal reasons.

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Preferably, the solution used to treat the surface under usage conditions is virtually not discernible after rinsing. Typical levels of cyclodextrin in usage compositions for usage conditions are from about 0.01% to about 5%, preferably from about 0.1% to about 4%, more preferably from about 0.5% to about 2% by weight of the composition. Compositions with higher concentrations are not needed in use. The presence of the surfactant can improve spreading and therefore coverage.

Concentrated compositions, however, can be used in order to deliver a less expensive product. When a concentrated product is used, i.e., when the level of cyclodextrin used is from about 3% to about 20%, more preferably from about 5% to about 10%, by weight of the concentrated composition, it is preferable to dilute the concentrated composition before treating surfaces. Preferably the concentrated cyclodextrin composition is diluted with about 50% to about 6000%, more preferably with about 75% to about 2000%, most preferably with about 100% to about 1000% by weight of the concentrated composition of water. The resulting diluted compositions have usage concentrations of cyclodextrin as discussed hereinbefore, e.g., of from about 0.1% to about 5%, by weight of the diluted composition.

(B). CYCLODEXTRIN-COMPATIBLE SURFACTANT

The cyclodextrin-compatible surfactant B., provides improved spreading and soil removal performance, as well as the cleaning of other undesirable materials from the food surfaces, food preparing surfaces and/or food containers, and the like. Furthermore, the composition containing a cyclodextrin-compatible surfactant can penetrate hydrophobic, oily soil better for improved pesticide removal and malodor control. For concentrated compositions, the surfactant facilitates the dispersion of many actives such as antimicrobial actives and perfumes in the concentrated aqueous compositions. The preferred surfactants are those which are food compatible.

The surfactant for use in providing the required low surface tension in the composition of the present invention should be cyclodextrin-compatible, that is it should not substantially form a complex with the cyclodextrin so as to diminish performance of the cyclodextrin and/or the surfactant. Complex formation diminishes both the ability of the cyclodextrin to absorb undesirable organic materials and the ability of the surfactant to lower the surface tension of the aqueous composition.

Suitable cyclodextrin-compatible surfactants can be readily identified by the absence of effect of cyclodextrin on the surface tension provided by the surfactant. This is achieved by determining the surface tension (in dyne/cm²) of aqueous solutions of the surfactant in the presence and in the absence of about 1% of a specific cyclodextrin in the solutions. The aqueous solutions contain surfactant at

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concentrations of approximately 0.5%, 0.1%, 0.01%, and 0.005%. The cyclodextrin can affect the surface activity of a surfactant by elevating the surface tension of the surfactant solution. If the surface tension at a given concentration in water differs by more than about 10% from the surface tension of the same surfactant in the 1% solution of the cyclodextrin, that is an indication of a strong interaction between the surfactant and the cyclodextrin. The preferred surfactants herein should have a surface tension in an aqueous solution that is different (lower) by less than about 10%, preferably less than about 5%, and more preferably less than about 1% from that of the same concentration solution containing 1% cyclodextrin.

Nonlimiting examples of cyclodextrin-compatible nonionic surfactants include block copolymers of ethylene oxide and propylene oxide. Suitable block polyoxyethylene-polyoxypropylene polymeric surfactants, that are compatible with most cyclodextrins, include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as the initial reactive hydrogen compound. Polymeric compounds made from a sequential ethoxylation and propoxylation of initial compounds with a single reactive hydrogen atom, such as C12-18 aliphatic alcohols, are not generally compatible with the cyclodextrin. Certain of the block polymer surfactant compounds designated Pluronic® and Tetronic® by the BASF-Wyandotte Corp., Wyandotte, Michigan, are readily available.

Nonlimiting examples of cyclodextrin-compatible surfactants of this type include:

<u>Pluronic Surfactants</u> with the general formula $H(EO)_n(PO)_m(EO)_nH$, wherein EO is an ethylene oxide group, PO is a propylene oxide group, and n and m are numbers that indicate the average number of the groups in the surfactants. Typical examples of cyclodextrin-compatible Pluronic surfactants are:

	Name	Average MW	Average n	Average m
	L-101	3,800	4	59
	L-81	2,750	3	42
30	L-44	2,200	10	23
	L-43	1,850	6	22
	F-38	4,700	43	16
	P-84	4,200	19	43,

and mixtures thereof.

35 <u>Tetronic Surfactants</u> with the general formula:

$$H(EO)n(PO)m$$
 (PO)m(EO)nH NCH_2CH_2N ((PO)m(EO)nH $(PO)m(EO)nH$

wherein EO, PO, n, and m have the same meanings as above. Typical examples of cyclodextrin-compatible Tetronic surfactants are:

5	Name	Average MW	Average n	Average m
9	901	4,700	3	18
9	908	25,000	114	22,

and mixtures thereof.

"Reverse" Pluronic and Tetronic surfactants have the following general 10 formulas:

Reverse Pluronic Surfactants H(PO)_m(EO)_n(PO)_mH
Reverse Tetronic Surfactants

$$H(PO)n(EO)m$$
 (EO)m(PO)nH NCH_2CH_2N (EO)m(PO)nH (EO)m(PO)nH

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wherein EO, PO, n, and m have the same meanings as above. Typical examples of cyclodextrin-compatible Reverse Pluronic and Reverse Tetronic surfactants are:

Reverse Pluronic surfactants:

	Name	Average MW	Average n	Average m		
20	10 R5	1,950	8	22		
	25 R1	2,700	21	6		
	Reverse Tetr	Reverse Tetronic surfactants				
	Name	Average MW	Average n	Average m		
	130 R2	7,740	9	26		
25	70 R2	3,870	4	13		
	and mixtures thereof.					

A preferred class of cyclodextrin-compatible nonionic surfactants are the polyalkyleneoxide polysiloxanes having a dimethyl polysiloxane hydrophobic moiety and one or more hydrophilic polyalkylene side chains and have the general formula:

30 R^1 — $(CH_3)_2SiO$ — $[(CH_3)_2SiO]_a$ — $[(CH_3)(R^1)SiO]_b$ — $Si(CH_3)_2$ — R^1 wherein a+b are from about 1 to about 50, preferably from about 3 to about 30, more preferably from about 10 to about 25, and each R^1 is the same or different and is

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selected from the group consisting of methyl and a poly(ethyleneoxide/propyleneoxide) copolymer group having the general formula:

$$-(CH_2)_n O(C_2 H_4 O)_c (C_3 H_6 O)_d R^2$$

with at least one R¹ being a poly(ethyleneoxide/propyleneoxide) copolymer group, and wherein n is 3 or 4, preferably 3; total c (for all polyalkyleneoxy side groups) has a value of from 1 to about 100, preferably from about 6 to about 100; total d is from 0 to about 14, preferably from 0 to about 3; and more preferably d is 0; total c+d has a value of from about 5 to about 150, preferably from about 9 to about 100 and each R² is the same or different and is selected from the group consisting of hydrogen, an alkyl having 1 to 4 carbon atoms, and an acetyl group, preferably hydrogen and methyl group.

Examples of this type of surfactants are the Silwet[®] surfactants which are available OSi Specialties, Inc., Danbury, Connecticut. Representative Silwet surfactants are as follows.

15	Name	Average MW	Average a+b	Average total c
	L-7608	600	1	9
	L-7607	1,000	2	17
	L-77	600	1	9
	L-7605	6,000	20	99
20	L-7604	4,000	21	53
	L-7600	4,000	11,	68
	L-7657	5,000	20	76
	L-7602	3,000	20	29
20	L-77 L-7605 L-7604 L-7600 L-7657	600 6,000 4,000 4,000 5,000	1 20 21 11 20	9 99 53 68 76

The molecular weight of the polyalkyleneoxy group (R¹) is less than or equal to about 10,000. Preferably, the molecular weight of the polyalkyleneoxy group is less than or equal to about 8,000, and most preferably ranges from about 300 to about 5,000. Thus, the values of c and d can be those numbers which provide molecular weights within these ranges. However, the number of ethyleneoxy units (-C₂H₄O) in the polyether chain (R¹) must be sufficient to render the polyalkyleneoxide polysiloxane water dispersible or water soluble. If propyleneoxy groups are present in the polyalkylenoxy chain, they can be distributed randomly in the chain or exist as blocks. Preferred Silwet surfactants are L-7600, L-7602, L-7604, L-7605, L-7657, and mixtures thereof.

The preparation of polyalkyleneoxide polysiloxanes is well known in the art. Polyalkyleneoxide polysiloxanes of the present invention can be prepared according

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to the procedure set forth in U.S. Pat. No. 3,299,112, incorporated herein by reference. Typically, polyalkyleneoxide polysiloxanes of the surfactant blend of the present invention are readily prepared by an addition reaction between a hydrosiloxane (i.e., a siloxane containing silicon-bonded hydrogen) and an alkenyl ether (e.g., a vinyl, allyl, or methallyl ether) of an alkoxy or hydroxy end-blocked polyalkylene oxide). The reaction conditions employed in addition reactions of this type are well known in the art and in general involve heating the reactants (e.g., at a temperature of from about 85° C. to 110° C.) in the presence of a platinum catalyst (e.g., chloroplatinic acid) and a solvent (e.g., toluene).

Nonlimiting examples of cyclodextrin-compatible anionic surfactants are the alkyldiphenyl oxide disulfonate, having the general formula:

$$SO_3Na$$
 SO_3Na

wherein R is an alkyl group. Examples of this type of surfactants are available from the Dow Chemical Company under the trade name Dowfax[®] wherein R is a linear or branched C_6 - C_{16} alkyl group. An example of these cyclodextrin-compatible anionic surfactant is Dowfax 3B2 with R being approximately a linear C_{10} group. These anionic surfactants are preferably not used when the antimicrobial active or preservative, etc., is cationic to minimize the interaction with the cationic actives, since the effect of both surfactant and cationic active are diminished.

The surfactants above are either weakly interactive with cyclodextrin (less than 5% elevation in surface tension, or non-interactive (less than 1% elevation in surface tension). Normal surfactants like sodium dodecyl sulfate and dodecanolpoly(6)ethoxylate are strongly interactive, with more than a 10% elevation in surface tension in the presence of a typical cyclodextrin like hydroxypropylbetacyclodextrin and methylated beta-cyclodextrin.

Typical levels of cyclodextrin-compatible surfactants in usage compositions are from about 0.01% to about 4%, preferably from about 0.03% to about 2%, more preferably from about 0.05% to about 1%, by weight of the composition. Typical levels of cyclodextrin-compatible surfactants in concentrated compositions are from about 0.1% to about 8%, preferably from about 0.2% to about 4%, more preferably from about 0.3% to about 3%, by weight of the concentrated composition.

(C). CYCLODEXTRIN-COMPATIBLE ANTIMICROBIAL ACTIVE

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The solubilized, water-soluble antimicrobial active, C., is useful in providing protection against organisms that become attached to food, food preparation surfaces and/or food containers. The antimicrobial should be cyclodextrin compatible, e.g., not substantially forming complexes with the cyclodextrin in the food cleaning composition. The free, uncomplexed antimicrobial, e.g., antibacterial, active provides an optimum antibacterial performance. The preferred antibacterials are those which are food compatible, e.g., suitable for direct or indirect food contact use and/or may be approved as GRAS, prior sanctioned, or subject to GRAS approval via a GRAS petition, for example, a new chemical developed for this invention.

Sanitization of food and food preparation and/or contact surfaces can be achieved by the compositions of the present invention containing antimicrobial materials, e.g., antibacterial halogenated compounds, quaternary compounds, and phenolic compounds.

Biguanides. Some of the more robust cyclodextrin-compatible antimicrobial halogenated compounds which can function as disinfectants/sanitizers as well as finish product preservatives (vide infra), and are useful in the compositions of the present invention can include 1,1'-hexamethylene bis(5-(p-chlorophenyl)biguanide), commonly known as chlorhexidine, and its salts, e.g., with hydrochloric, acetic and gluconic acids. The digluconate salt is highly water-soluble, about 70% in water, and the diacetate salt has a solubility of about 1.8% in water. When chlorhexidine is used as a sanitizer in the present invention it is typically present at a level of from about 0.001% to about 0.4%, preferably from about 0.002% to about 0.3%, and more preferably from about 0.05% to about 0.2%, by weight of the usage composition. In some cases, a level of from about 1% to about 2% may be needed for virucidal activity.

Other useful biguanide compounds include Cosmoci[®] CQ[®], Vantocil[®] IB, including poly (hexamethylene biguanide) hydrochloride. Other useful cationic antimicrobial agents include the bis-biguanide alkanes. Usable water soluble salts of the above are chlorides, bromides, sulfates, alkyl sulfonates such as methyl sulfonate and ethyl sulfonate, phenylsulfonates such as p-methylphenyl sulfonates, nitrates, acetates, gluconates, and the like.

Examples of suitable bis biguanide compounds are chlorhexidine; 1,6-bis-(2-ethylhexylbiguanidohexane)dihydrochloride; 1,6-di-(N_1 , N_1 '-phenyldiguanido- N_5 , N_5 ')-hexane tetrahydrochloride; 1,6-di-(N_1 , N_1 '-phenyl- N_1 , N_1 '-methyldiguanido- N_5 , N_5 ')-hexane dihydrochloride; 1,6-di(N_1 , N_1 '-o-chlorophenyldiguanido- N_5 , N_5 ')-hexane dihydrochloride; 1,6-di(N_1 , N_1 '-2,6-dichlorophenyldiguanido- N_5 , N_5 ')-hexane dihydrochloride; 1,6-di[N_1 , N_1 '-beta.-(p-methoxyphenyl) diguanido- N_5 , N_5 ']-hexane

1,6-di(N₁,N₁'-.alpha.-methyl-.beta.-phenyldiguanido-N₅,N₅')dihydrochloride; 1,6-di(N₁,N₁'-p-nitrophenyldiguanido-N₅,N₅')hexane dihydrochloride; hexane dihydrochloride;.omega.:.omega.'-di-(N1,N1'-phenyldiguanido-N5,N5')-di-ndihydrochloride;.omega:omega'-di(N1,N1'-p-chlorophenyldiguanidopropylether tetrahydrochloride; 1,6-di(N₁,N₁'-2,4-5 N₅,N₅')-di-n-propylether $1,6-di(N_1,N_1'-p$ dichlorophenyldiguanido-N5,N5')hexane tetrahydrochloride; 1,6-di(N₁,N₁'-2,4,5methylphenyldiguanido-N5,N5')hexane dihydrochloride; trichlorophenyldiguanido-N5,N5')hexane tetrahydrochloride; 1,6-di[N1,N1'-.alphaethyldiguanido-N5,N5'] hexane (p-chlorophenyl) dihydrochloride;.omega.:omega.'di(N₁, N₁'-p-chlorophenyldiguanido-N₅,N₅')m-10 xylene dihydrochloride; 1,12-di(N₁,N₁'-p-chlorophenyldiguanido-N₅,N₅') dodecane dihydrochloride; 1,10-di(N₁,N₁'-phenyldiguanido-N₅,N₅')-decane 1,12-di(N₁,N₁'-phenyldiguanido-N₅,N₅') tetrahydrochloride; dodecane tetrahydrochloride; 1,6-di(N₁,N₁'-o-chlorophenyldiguanido-N₅,N₅') hexane 1,6-di(N₁,N₁'-p-chlorophenyldiguanido-N₅,N₅')-hexane 15 dihydrochloride; tetrahydrochloride; ethylene bis (1-tolyl biguanide); ethylene bis (p-tolyl biguanide); biguanide); ethylene bis(p-tert-amylphenyl bis(3,5-dimethylphenyl biguanide); ethylene bis(nonylphenyl biguanide); ethylene bis (phenyl biguanide); ethylene bis (N-butylphenyl biguanide); ethylene bis (2,5-diethoxyphenyl biguanide); ethylene bis(2,4-dimethylphenyl biguanide); ethylene bis(o-diphenylbiguanide); 20 ethylene bis(mixed amyl naphthyl biguanide); N-butyl ethylene bis(phenylbiguanide); trimethylene bis(o-tolyl biguanide), N-butyl trimethylene bis(phenyl biguanide); and the corresponding pharmaceutically acceptable salts of all of the above such as the acetates; gluconates; hydrochlorides; hydrobromides; citrates; bisulfites; fluorides; phosphites; N-coconutalkylsarcosinates; hypophosphites; 25 polymaleates; perfluorooctanoates; silicates; sorbates; salicylates; maleates; tartrates; fumarates; ethylenediaminetetraacetates; iminodiacetates; cinnamates; thiocyanates; arginates; pyromellitates; tetracarboxybutyrates; benzoates; glutarates; monofluorophosphates; and perfluoropropionates, and mixtures thereof. Preferred antimicrobials from this group are 1,6-di-(N₁,N₁'-phenyldiguanido-N₅,N₅')-hexane tetrahydrochloride; 1,6-30 $di(N_1,N_1'-o-chlorophenyldiguanido-N_5,N_5')-hexane dihydrochloride; 1,6-di(N_1,N_1'-o-chlorophenyldiguanido-N_5,N_5')-hexane dihydrochloride; 1,6-di(N_1,N_1'-o-chlorophenyldiguanido-N_5,N_5'-o-chlorophenyldiguanido-N_5,N_5'-o-chlorophenyldiguanido-N_5,N_5'-o-chlorop$ $2,6-dichlorophenyldiguanido-N_5,N_5') hexane \\ dihydrochloride; \\ 1,6-di(N_1,N_1'-2,4-1) hexane \\ dihydroc$ dichlorophenyldiguanido-N5, N5') hexane tetrahydrochloride; 1,6-di[N1,N1'-.alpha.ethyldiguanido-N5,N5'] hexane (p-chlorophenyl) N₁'-p-chlorophenyldiguanido-N₅,N₅')mdihydrochloride;.omega.:omega.'di(N1, 35 xylene dihydrochloride; 1,12-di(N₁,N₁'-p-chlorophenyldiguanido-N₅,N₅') dodecane 1,6-di(N₁,N₁'-o-chlorophenyldiguanido-N₅,N₅') dihydrochloride; hexane

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1,6-di(N₁,N₁'-p-chlorophenyldiguanido-N₅,N₅')-hexane dihydrochloride; tetrahydrochloride; and mixtures thereof; more preferably, 1,6-di(N₁,N₁'-odihydrochloride; 1,6-di(N₁,N₁'-2,6chlorophenyldiguanido-N5,N5')-hexane 1,6-di(N₁,N₁'-2,4dihydrochloride; dichlorophenyldiguanido-N5,N5')hexane dichlorophenyldiguanido-N5,N5')hexane tetrahydrochloride; 1,6-di[N1,N1'-.alpha.-(p-chlorophenyl) ethyldiguanido-N5,N5'] hexane N₁'-p-chlorophenyldiguanido-N₅,N₅')mdihydrochloride;.omega.:.omega.'di(N1, xylene dihydrochloride; 1,12-di(N₁,N₁'-p-chlorophenyldiguanido-N₅,N₅') dodecane 1,6-di(N₁,N₁'-o-chlorophenyldiguanido-N₅,N₅') dihydrochloride; 1,6-di(N_1,N_1 '-p-chlorophenyldiguanido- N_5,N_5 ')-hexane dihydrochloride; tetrahydrochloride; and mixtures thereof. As stated hereinbefore, the bis biguanide of choice is chlorhexidine its salts, e.g., digluconate, dihydrochloride, diacetate, and mixtures thereof.

Quaternary Compounds. A wide range of quaternary compounds can also be used as antimicrobial actives, in conjunction with the preferred surfactants. Nonlimiting examples of useful quaternary compounds include: (1) benzalkonium chlorides and/or substituted benzalkonium chlorides such as commercially available Barquat® (available from Lonza), Maquat® (available from Mason), Variquat® (available from Witco/Sherex), and Hyamine® (available from Lonza); (2) dialkyl quaternary such as Bardac® products of Lonza, (3) N-(3-chloroallyl) hexaminium chlorides such as Dowicide® and Dowicil® available from Dow; (4) benzethonium chloride such as Hyamine® 1622 from Rohm & Haas; (5) methylbenzethonium chloride represented by Hyamine® 10X supplied by Rohm & Haas, (6) cetylpyridinium chloride such as Cepacol chloride available from of Merrell Labs. Typical concentrations for biocidal effectiveness of these quaternary compounds range from about 0.001% to about 0.8%, preferably from about 0.005% to about 0.3%, more preferably from about 0.01% to 0.2%, by weight of the usage composition. The corresponding concentrations for the concentrated compositions are from about 0.003% to about 2%, preferably from about 0.006% to about 1.2%, and more preferably from about 0.1% to about 0.8% by weight of the concentrated compositions.

The surfactants, when added to the antimicrobials tend to provide improved antimicrobial action. This is especially true for the siloxane surfactants, and especially when the siloxane surfactants are combined with the chlorhexidine antimicrobial actives.

(D). SEQUESTRANT/BUILDER

The preferred sequestrant and/or builder herein is polyphosphate salt or organic polycarboxylic salt, e.g., sodium and/or potassium citrate, and/or sodium and/or potassium ethylenediaminetetraacetate, which are standard items of commerce and are or may be approved as GRAS. Other organic polycarboxylic acids, especially those that are or may be approved as GRAS, such as citric, tartaric, malic, etc. acids, can also be used. A preferred version of polyphosphate is an anhydrous Fast Dissolving STPP manufactured by the FMC corporation. Complex phosphates such as sodium hexametaphosphate can also be used, and phosphates are useful to maintain the clarity of dilute solutions made from hard water. Typically, the sequestrant/builder is present at a level of from about 0.0005% to about 3%, preferably from about 0.005% to about 0.5%, and more preferably from about 0.01% to about 0.2%, by weight of the dilute composition. Sequestrant/builders can help maintain the efficacy of the formulas in the presence of hardness. Additionally, other buffer/builders may be used. Potassium/sodium carbonate and/or versions of potassium/sodium ortho-phosphate are convenient and may provide additional pH control.

(E). PERFUME

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The food cleaning composition of the present invention can also optionally provide a "scent signal" in the form of a pleasant odor which signals the removal of undesirable materials from food and/or food contacting surfaces. Any type of food compatible perfume can be incorporated into the composition of the present invention. One preferred type are perfume compositions that provide various fruity odors. The scent signal is designed to provide a fleeting perfume scent, and is not designed to be overwhelming or to be used as an odor masking ingredient. When perfume is added as a scent signal, it is added only at very low levels, e.g., from about 0% to about 0.5%, preferably from about 0.003% to about 0.3%, more preferably from about 0.005% to about 0.2%, by weight of the usage composition.

Perfume can also be added as a more intense odor in product and on surfaces. When stronger levels of perfume are preferred, relatively higher levels of perfume can be added. It is essential, however, that the perfume be added at a level wherein even if all of the perfume in the composition were to complex with the cyclodextrin molecules, there will still be an effective level of uncomplexed cyclodextrin molecules present in the solution to provide adequate removal of undesirable materials and/or odor control. In order to reserve an effective amount of cyclodextrin molecules for removal of undesirable materials and/or odor control, perfume is typically present at a level wherein less than about 90% of the cyclodextrin complexes with the perfume, preferably less than about 50% of the cyclodextrin complexes with the perfume, more

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preferably, less than about 30% of the cyclodextrin complexes with the perfume, and most preferably, less than about 10% of the cyclodextrin complexes with the perfume. The cyclodextrin to perfume weight ratio should be greater than about 8:1, preferably greater than about 10:1, more preferably greater than about 20:1, even more preferably greater than 40:1 and most preferably greater than about 70:1.

Preferably the perfume is hydrophilic and is composed predominantly of ingredients selected from two groups of ingredients, namely, (a) hydrophilic ingredients having a ClogP of less than about 3.5, more preferably less than about 3.0, and (b) ingredients having significant low detection threshold, and mixtures thereof. Typically, at least about 50%, preferably at least about 60%, more preferably at least about 70%, and most preferably at least about 80% by weight of the perfume is composed of perfume ingredients of the above groups (a) and (b). For these preferred perfumes, the cyclodextrin to perfume weight ratio is typically of from about 2:1 to about 200:1; preferably from about 4:1 to about 100:1, more preferably from about 6:1 to about 50:1, and even more preferably from about 8:1 to about 30:1.

(a). Hydrophilic Perfume Ingredients

The hydrophilic perfume ingredients are more soluble in water, have less of a tendency to complex with the cyclodextrins, and are more available in the food cleaning composition than the ingredients of conventional perfumes. The hydrophilic perfume ingredients can also be more readily rinsed off and removed from the food and food contacting surfaces, and do not leave a high level of residue on said surfaces which can be hydrophobic surfaces. The degree of hydrophobicity of a perfume ingredient can be correlated with its octanol/water partition coefficient P. The octanol/water partition coefficient of a perfume ingredient is the ratio between its equilibrium concentration in octanol and in water. A perfume ingredient with a greater partition coefficient P is considered to be more hydrophobic. Conversely, a perfume ingredient with a smaller partition coefficient P is considered to be more hydrophobic. Since the partition coefficients of the perfume ingredients normally have high values, they are more conveniently given in the form of their logarithm to the base 10, logP. Thus the preferred perfume hydrophilic perfume ingredients of this invention have logP of about 3.5 or smaller, preferably of about 3.0 or smaller.

The logP of many perfume ingredients have been reported; for example, the Pomona92 database, available from Daylight Chemical Information Systems, Inc. (Daylight CIS), Irvine, California, contains many, along with citations to the original literature. However, the logP values are most conveniently calculated by the "CLOGP" program, also available from Daylight CIS. This program also lists

experimental logP values when they are available in the Pomona92 database. The "calculated logP" (ClogP) is determined by the fragment approach of Hansch and Leo (cf., A. Leo, in Comprehensive Medicinal Chemistry, Vol. 4, C. Hansch, P. G. Sammens, J. B. Taylor and C. A. Ramsden, Eds., p. 295, Pergamon Press, 1990, incorporated herein by reference). The fragment approach is based on the chemical structure of each perfume ingredient, and takes into account the numbers and types of atoms, the atom connectivity, and chemical bonding. The ClogP values, which are the most reliable and widely used estimates for this physicochemical property, are used instead of the experimental logP values in the selection of perfume ingredients which are useful in the present invention.

Non-limiting examples of the more preferred hydrophilic perfume ingredients are allyl amyl glycolate, allyl caproate, amyl acetate, amyl propionate, anisic aldehyde, anisyl acetate, anisole, benzaldehyde, benzyl acetate, benzyl acetone, benzyl alcohol, benzyl formate, benzyl iso valerate, benzyl propionate, beta gamma hexenol. calone, camphor gum, laevo-carveol, d-carvone, laevo-carvone, cinnamic alcohol, cinnamyl acetate, cinnamic alcohol, cinnamyl formate, cinnamyl propionate, cisjasmone, cis-3-hexenyl acetate, coumarin, cuminic alcohol, cuminic aldehyde, Cyclal C, cyclogalbanate, dihydroeuginol, dihydro isojasmonate, dimethyl benzyl carbinol, dimethyl benzyl carbinyl acetate, ethyl acetate, et ethyl anthranilate, ethyl benzoate, ethyl butyrate, ethyl cinnamate, ethyl hexyl ketone, ethyl maltol, ethyl-2-methyl butyrate, ethyl methylphenyl glycidate, ethyl phenyl acetate, ethyl salicylate, ethyl vanillin, eucalyptol, eugenol, eugenyl acetate, eugenyl formate, eugenyl methyl ether, fenchyl alcohol, flor acetate (tricyclo decenyl acetate), fructone, frutene (tricyclo decenyl propionate), geraniol, geranyl oxyacetaldehyde, heliotropin, hexenol, hexenyl acetate, hexyl acetate, hexyl formate, hinokitiol, hydratropic alcohol. hydroxycitronellal, hydroxycitronellal diethyl hydroxycitronellol, indole, isoamyl alcohol, iso cyclo citral, isoeugenol, isoeugenyl acetate, isomenthone, isopulegyl acetate, isoquinoline, keone, ligustral, linalool, linalool oxide, linalyl formate, lyral, menthone, methyl acetophenone, methyl amyl ketone, methyl anthranilate, methyl benzoate, methyl benzyl acetate, methyl cinnamate, methyl dihydrojasmonate, methyl eugenol, methyl heptenone, methyl heptine carbonate, methyl heptyl ketone, methyl hexyl ketone, methyl isobutenyl tetrahydropyran, methyl-N-methyl anthranilate, methyl beta naphthyl ketone, methyl phenyl carbinyl acetate, methyl salicylate, nerol, nonalactone, octalactone, octyl alcohol (octanol-2), para-anisic aldehyde, para-cresol, para-cresyl methyl ether, para hydroxy phenyl butanone, para-methoxy acetophenone, para-methyl acetophenone, phenoxy ethanol, phenoxyethyl propionate, phenyl acetaldehyde, phenylacetaldehyde

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diethyl ether, phenylethyl oxyacetaldehyde, phenyl ethyl acetate, phenyl ethyl alcohol, phenyl ethyl dimethyl carbinol, prenyl acetate, propyl butyrate, pulegone, rose oxide, safrole, terpineol, vanillin, viridine, and mixtures thereof.

Nonlimiting examples of other preferred hydrophilic perfume ingredients which can be used in perfume compositions of this invention are allyl heptoate, amyl benzoate, anethole, benzophenone, carvacrol, citral, citronellol, citronellyl nitrile, cyclohexyl ethyl acetate, cymal, 4-decenal, dihydro isojasmonate, dihydro myrcenol, ethyl methyl phenyl glycidate, fenchyl acetate, florhydral, gamma-nonalactone, geranyl formate, geranyl nitrile, hexenyl isobutyrate, alpha-ionone, isobornyl acetate, isobutyl benzoate, isononyl alcohol, isomenthol, para-isopropyl phenylacetaldehyde, isopulegol, linalyl acetate, 2-methoxy naphthalene, menthyl acetate, methyl chavicol, musk ketone, beta naphthol methyl ether, neral, nonyl aldehyde, phenyl heptanol, phenyl hexanol, terpinyl acetate, Veratrol, yara-yara, and mixtures thereof.

The preferred perfume compositions used in the present invention contain at least 4 different hydrophilic perfume ingredients, preferably at least 5 different hydrophilic perfume ingredients, more preferably at least 6 different hydrophilic perfume ingredients, and even more preferably at least 7 different hydrophilic perfume ingredients. Most common perfume ingredients which are derived from natural sources are composed of a multitude of components. When each such material is used in the formulation of the preferred perfume compositions of the present invention, it is counted as one single ingredient, for the purpose of defining the invention.

(b). Low Odor Detection Threshold Perfume Ingredient

The odor detection threshold of an odorous material is the lowest vapor concentration of that material which can be olfactorily detected. The odor detection threshold and some odor detection threshold values are discussed in, e.g., "Standardized Human Olfactory Thresholds", M. Devos et al, IRL Press at Oxford University Press, 1990, and "Compilation of Odor and Taste Threshold Values Data", F. A. Fazzalari, editor, ASTM Data Series DS 48A, American Society for Testing and Materials, 1978, both of said publications being incorporated by reference. The use of small amounts of perfume ingredients that have low odor detection threshold values can improve perfume odor character, even though they are not as hydrophilic as perfume ingredients of group (a) which are given hereinabove. Perfume ingredients that do not belong to group (a) above, but have a significantly low detection threshold, useful in the composition of the present invention, are selected from the group consisting of ambrox, bacdanol, benzyl salicylate, butyl anthranilate, cetalox, damascenone, alpha-damascone, gamma-dodecalactone, ebanol,

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herbavert, cis-3-hexenyl salicylate, alpha-ionone, beta-ionone, alpha-isomethylionone, lilial, methyl nonyl ketone, gamma-undecalactone, undecylenic aldehyde, and mixtures thereof. These materials are preferably present at low levels in addition to the hydrophilic ingredients of group (a), typically less than about 20%, preferably less than about 15%, more preferably less than about 10%, by weight of the total perfume compositions of the present invention. However, only low levels are required to provide an effect.

There are also hydrophilic ingredients of group (a) that have a significantly low detection threshold, and are especially useful in the composition of the present invention. Examples of these ingredients are allyl amyl glycolate, anethole, benzyl acetone, calone, cinnamic alcohol, coumarin, cyclogalbanate, Cyclal C, cymal, 4-decenal, dihydro isojasmonate, ethyl anthranilate, ethyl-2-methyl butyrate, ethyl methylphenyl glycidate, ethyl vanillin, eugenol, flor acetate, florhydral, fructone, frutene, heliotropin, keone, indole, iso cyclo citral, isoeugenol, lyral, methyl heptine carbonate, linalool, methyl anthranilate, methyl dihydrojasmonate, methyl isobutenyl tetrahydropyran, methyl beta naphthyl ketone, beta naphthol methyl ether, nerol, para-anisic aldehyde, para hydroxy phenyl butanone, phenyl acetaldehyde, vanillin, and mixtures thereof. Use of low odor detection threshold perfume ingredients minimizes the level of organic material that is released into the atmosphere.

20 (F). LOW MOLECULAR WEIGHT POLYOLS

Low molecular weight polyols with relatively high boiling points, as compared to water, such as ethylene glycol, propylene glycol and/or diethylene glycol are preferred optional ingredients for improving organic residue removal and/or odor control performance of the composition of the present invention. Not to be bound by theory, it is believed that the incorporation of a small amount of low molecular weight glycols into the composition of the present invention enhances the formation of the cyclodextrin inclusion complexes with small organic molecules. The addition of the glycols is believed to fill up void space in the cyclodextrin cavity that is unable to be filled by some organic residue molecules of relatively smaller sizes. Preferably the glycol used is glycerine, ethylene glycol, propylene glycol, dipropylene glycol or mixtures thereof, more preferably diethylene glycol and propylene glycol. Cyclodextrins prepared by processes that result in a level of such polyols are highly desirable, since they can be used without removal of the polyols.

Some polyols, e.g., dipropylene glycol, are also useful to facilitate the solubilization of some perfume ingredients in the composition of the present invention.

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Typically, glycol is added to the composition of the present invention at a level of from about 0.01% to about 3%, by weight of the composition, preferably from about 0.05% to about 1%, more preferably from about 0.1% to about 0.5%, by weight of the composition. The preferred weight ratio of low molecular weight polyol to cyclodextrin is from about 2:1,000 to about 20:100, more preferably from about 3:1,000 to about 15:100, even more preferably from about 5:1,000 to about 10:100, and most preferably from about 1:100 to about 7:100.

(G). OPTIONAL AMINOCARBOXYLATE CHELATORS

Chelators, e.g., ethylenediaminetetraacetic acid (EDTA), hydroxyethylenediaminetriacetic acid, diethylenetriaminepentaacetic acid, and other aminocarboxylate chelators, and mixtures thereof, and their salts, and mixtures thereof, can optionally be used to increase antimicrobial and preservative effectiveness against Gramnegative bacteria, especially Pseudomonas species. Although sensitivity to EDTA and other aminocarboxylate chelators is mainly a characteristic of Pseudomonas species, other bacterial species highly susceptible to chelators include Achromobacter, Alcaligenes, Azotobacter, Escherichia, Salmonella, Spirillum, and Vibrio. Other groups of organisms also show increased sensitivities to these chelators, including fungi and yeasts. Furthermore, aminocarboxylate chelators can help, e.g., maintaining product clarity, protecting fragrance and perfume components, and preventing rancidity and off odors.

Although these aminocarboxylate chelators may not be potent biocides in their own right, they function as potentiators for improving the performance of other antimicrobials/preservatives in the compositions of the present invention. Aminocarboxylate chelators can potentiate the performance of many of the cationic, anionic, and nonionic antimicrobials/preservatives, phenolic compounds, and isothiazolinones, that are used as antimicrobials/preservatives in the composition of the present invention. Nonlimiting examples of cationic antimicrobials/ preservatives potentiated by aminocarboxylate chelators in solutions are chlorhexidine salts (including digluconate, diacetate, and dihydrochloride salts), benalkonium chloride, cetrimonium, myristalkonium chloride, cetylpyridinium chloride, lauryl pyridinium of useful the like. Nonlimiting examples antimicrobials/preservatives which are enhanced by aminocarboxylate chelators are sorbic acid and potassium sorbate.

The optional chelators are present in the compositions of this invention at levels of, typically, from about 0.01% to about 0.3%, more preferably from about 0.02% to about 0.1%, most preferably from about 0.02% to about 0.05% by weight of the usage compositions to provide antimicrobial efficacy in this invention.

Free, uncomplexed aminocarboxylate chelators are required to potentiate the efficacy of the antimicrobials. Thus, when excess alkaline earth (especially calcium and magnesium) and transitional metals (iron, manganese, copper, and others) are present, free chelators are not available and antimicrobial potentiation is not observed. In the case where significant water hardness or transitional metals are available or where product esthetics require a specified chelator level, higher levels may be required to allow for the availability of free, uncomplexed aminocarboxylate chelators to function as antimicrobial/preservative potentiators. It is more preferred that the water carrier used in the composition is free or low in hardness ions, thus distilled or deionized water are preferred, as disclosed herein below.

(H). SUDS SUPPRESSORS

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At low levels, suds suppressors or antifoamers can be used, especially in the case where a certain surfactant level is desired for wetting and/or efficacy, but the degree of foam generated in the washing of produce is desired to be kept low. The amount of suds suppresser can be tailored in conjunction with the type and level of surfactant used. Preferred suds suppressors include silicones and their derivatives. Preferably food grade suds suppressors are used, with DC-1500 and its derivatives, such as DC-4270 and DC2-4242, from Dow Corning being useful suds suppressors. Some polyoxyalkylene polysiloxane silicone surfactants and polyoxyethylene-polyoxypropylene block copolymeric surfactants having low content of oxyethylene monomers, typically least than about 20%, preferably less than 15%, can function as suds suppressors. Typically suds suppressor is present at a level of from about 0.01% to about 2%, preferably from about 0.05% to about 1%, more preferably from about 0.1% to about 0.5%, by weight of the usage composition.

In some applications, it is actually preferred to apply a foaming food cleaning composition onto food and/or food contacting surfaces. For such applications, one normally provides an article of manufacture, suitable for use by an individual to clean food surfaces and/or food preparation and food contact surfaces, containing a food compatible cleaning solution that is capable of being dispensed with a clearly visible content of foam from said container, the foam preferably remaining visible for at least 3 seconds optionally for at least 1 minute. The article can comprises a foaming spray head and is preferably of the trigger-type. The food compatible cleaning solution optionally comprises a non-detergent cyclodextrin compatible foam enhancing component, optionally selected from polymeric shear-thinning thickeners, optionally at a level of from about 0.001% to about 1%, preferably from about 0.005% to about 0.5%. The polymeric shear thinning thickeners are typically selected from the group consisting of substituted celluloses, modified polysaccharides, and naturally occurring

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gums, e.g., from about 0.001% to about 1% of xanthan gum. The cleaning solution preferably comprises all food compatible ingredients. The toxicologically acceptable cleaning solution, in one embodiment, comprises:

- (a) from about 0.1 % to about 5%, by weight of solubilized, uncomplexed cyclodextrin;
- (b) optionally, from about 0.1% to about 4%, by weight of cyclodextrin compatible surfactant;
- (c) optionally, from about 0.001% to about 0.5%, by weight of cyclodextrin compatible antimicrobial active;
- (d) optionally, from about 0.001% to about 0.5%, by weight of perfume;
- (e) optionally, from about 0.01% to about 5%, by weight of metallic salts;
- optionally, from about 0.1% to about 4% by weight of cyclodextrin compatible organic polycarboxylic acid;
- (g) optionally, cyclodextrin compatible preservative;
- 15 (h) optionally, at least about 0.05%, by weight, of water-soluble polyethylene glycol having a molecular weight of about 200, or higher; and
 - (i) the balance comprising an aqueous carrier selected from water and, optionally, low molecular weight, food compatible organic solvent;
- said cleaning solution preferably containing only food compatible ingredients, and being capable of being dispensed with a clearly visible content of foam from said container.

The method for cleaning food and/or food contacting surfaces using a visible foam can be advantageous, since it helps the user see what areas have been treated, thus helping insure complete treatment of all areas while avoiding overtreatment of any specific area.

(I). METAL SALTS

Optionally, but highly preferred, the present invention can include metallic salts for added odor absorption and/or antimicrobial benefit for the cyclodextrin solution. The metallic salts are selected from the group consisting of copper salts, zinc salts, and mixtures thereof.

Copper salts have some antimicrobial benefits. Specifically, cupric abietate acts as a fungicide, copper acetate acts as a mildew inhibitor, cupric chloride acts as a fungicide, copper lactate acts as a fungicide, and copper sulfate acts as a germicide. Copper salts also possess some malodor control abilities. See U. S. Pat. No. 3,172,817, Leupold, et al., which discloses deodorizing compositions for treating disposable articles, comprising at least slightly water-soluble salts of acylacetone,

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including copper salts and zinc salts, all of said patents are incorporated herein by reference.

The preferred zinc salts possess malodor control abilities. Zinc has been used most often for its ability to ameliorate malodor, e.g., in mouth wash products, as disclosed in U.S. Pat. Nos. 4,325,939, issued Apr. 20, 1982 and 4,469,674, issued Sept. 4, 1983, to N. B. Shah, et al., all of which are incorporated herein by reference. Highly-ionized and soluble zinc salts such as zinc chloride, provide the best source of zinc ions. Zinc borate functions as a fungistat and a mildew inhibitor, zinc caprylate functions as a fungicide, zinc chloride provides antiseptic and deodorant benefits, zinc ricinoleate functions as a fungicide, zinc sulfate heptahydrate functions as a fungicide and zinc undecylenate functions as a fungistat.

Preferably the metallic salts are water-soluble zinc salts, copper salts or mixtures thereof, and more preferably zinc salts, especially ZnCl₂. These salts are preferably present in the present invention primarily to absorb amine and sulfur-containing compounds that have molecular sizes too small to be effectively complexed with the cyclodextrin molecules. Low molecular weight sulfur-containing materials, e.g., sulfide and mercaptans, are components of many types of food odors, e.g., garlic, onion, cabbage, spoiled meat, etc. Low molecular weight amines are also components of many food odors, such as fish odor, etc.

When metallic salts are added to the composition of the present invention they are typically present at a level of from about 0.1% to about 10%, preferably from about 0.2% to about 8%, more preferably from about 0.3% to about 5% by weight of the usage composition. When zinc salts are used as the metallic salt, and a clear solution is desired, it is preferable that the pH of the solution is adjusted to less than about 7, more preferably less than about 6, most preferably, less than about 5, in order to keep the solution clear.

(J). ENZYMES

Enzymes can be used to remove certain types of soils on food, especially degraded protein materials, glycoproteins, fruit resins, and the like. Enzymes can digest some soil and help both in the removal of the soil and the diffusion and/or penetration of other actives such as cyclodextrin and/or antimicrobial actives, to improve their performance. Proteases and amylases are especially desirable. The activity of commercial enzymes depends very much on the type and purity of the enzyme being considered. Enzymes that are water soluble proteases like pepsin, tripsin, ficin, bromelin, papain, rennin, and mixtures thereof are particularly useful.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, preferably from about 0.001 mg to about 3 mg, more preferably

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from about 0.002 mg to about 1 mg, of active enzyme per gram of the aqueous compositions. Stated otherwise, the aqueous compositions herein can comprise from about 0.0001% to about 0.5%, preferably from about 0.001% to about 0.3%, more preferably from about 0.005% to about 0.2% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.0005 to 0.1 Anson units (AU) of activity per gram of aqueous composition.

Nonlimiting examples of suitable, commercially available, water soluble proteases are pepsin, tripsin, ficin, bromelin, papain, rennin, and mixtures thereof. Papain can be isolated, e.g., from papaya latex, and is available commercially in the purified form of up to, e.g., about 80% protein, or cruder, technical grade of much lower activity. Other suitable examples of proteases are the subtilisins which are obtained from particular strains of B. subtilis and B. licheniforms. Another suitable protease is obtained from a strain of Bacillus, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based soils that are commercially available include those sold under the trade names ALCALASE® and SAVINASE® by Novo Industries A/S (Denmark) and MAXATASE® by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985); Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985); and proteases made by Genencor International, Inc., according to one or more of the following patents: Caldwell et al, U.S. Patent Nos. 5,185,258, 5,204,015 and 5,244,791.

A wide range of enzyme materials and means for their incorporation into liquid compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985. Other enzyme materials useful for liquid formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868, Hora et al, issued April 14, 1981. Enzymes can be stabilized by various techniques, e.g., those disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al., European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas, and in U.S. Patent

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3,519,570. All of the above patents and applications are incorporated herein, at least in pertinent part.

Enzyme-polyethylene glycol conjugates are also preferred. Such polyethylene glycol (PEG) derivatives of enzymes, wherein the PEG or alkoxy-PEG moieties are coupled to the protein molecule through, e.g., secondary amine linkages. Suitable derivatization decreases immunogenicity, thus minimizes allergic reactions, while still maintains some enzymatic activity. An example of protease-PEG's is PEG-subtilisin Carlsberg from B. *lichenniformis* coupled to methoxy-PEGs through secondary amine linkage, and is available from Sigma-Aldrich Corp., St. Louis, Missouri.

(K). ANTIMICROBIAL PRESERVATIVES

Optionally, but preferably, solubilized, water-soluble, antimicrobial preservative can be added to the composition of the present invention if the antimicrobial material C. is not sufficient, or is not present, because cyclodextrin molecules are made up of varying numbers of glucose units which can be consumed by certain microorganisms, especially when in aqueous compositions. This drawback can lead to the problem of storage stability of cyclodextrin solutions for any significant length of time. Contamination by certain microorganisms with subsequent microbial growth can result in an unsightly and/or malodorous solution. Because microbial growth in cyclodextrin solutions is highly objectionable when it occurs, it is highly preferable to include a solubilized, water-soluble, antimicrobial preservative, which is effective for inhibiting and/or regulating microbial growth in order to increase storage stability of the preferably clear, aqueous odor-absorbing solution containing water-soluble cyclodextrin.

Typical microorganisms that can be found in cyclodextrin supplies and whose growth can be found in the presence of cyclodextrin in aqueous cyclodextrin solutions include bacteria, e.g., <u>Bacillus thuringiensis</u> (cereus group) and <u>Bacillus sphaericus</u>; and fungi, e.g., <u>Aspergillus ustus</u>. <u>Bacillus sphaericus</u> is one of the most numerous members of <u>Bacillus</u> species in soils. <u>Aspergillus ustus</u> is common in grains and flours which are raw materials to produce cyclodextrins. Microorganisms such as <u>Escherichia coli</u> and <u>Pseudomonas aeruginosa</u> are found in some water sources, and can be introduced during the preparation of cyclodextrin solutions. Other <u>Pseudomonas</u> species, such as <u>P. cepacia</u>, are typical microbial contaminants in surfactant manufacturing facilities and may readily contaminate packed finished products. Typical other bacterial contaminants may include <u>Burkholderia</u>, <u>Enterobacter</u> and <u>Gluconobacter</u> species. Representative fungal species which may be associated with agricultural soils, crops and in the case of this invention, corn

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products such as cyclodextrins include <u>Aspergillus</u>, <u>Absidia</u>, <u>Penicillium</u>, <u>Paecilomyces</u>, and other species.

It is preferable to use a broad spectrum preservative, e.g., one that is effective on both bacteria (both gram positive and gram negative) and fungi. A limited spectrum preservative, e.g., one that is only effective on a single group of microorganisms, e.g., fungi, can be used in combination with a broad spectrum preservative or other limited spectrum preservatives with complimentary and/or supplementary activity. A mixture of broad spectrum preservatives can also be used. In some cases where a specific group of microbial contaminants is problematic (such as Gram negatives), aminocarboxylate chelators may be used alone or as potentiators in conjunction with other preservatives. These chelators which include, e.g., ethylenediaminetetraacetic acid (EDTA), hydroxyethylenediaminetriacetic acid, diethylenetriaminepentaacetic acid, and other aminocarboxylate chelators, and mixtures thereof, and their salts, and mixtures thereof, can increase preservative effectiveness against Gram-negative bacteria, especially *Pseudomonas* species, as disclosed herein before.

Antimicrobial preservatives useful in the present invention include biocidal compounds, i.e., substances that kill microorganisms, or biostatic compounds, i.e., substances that inhibit and/or regulate the growth of microorganisms. antimicrobial preservatives are those that are water-soluble and are effective at low levels because the organic preservatives can form inclusion complexes with the cyclodextrin molecules and compete with the organic residue molecules for the cyclodextrin cavities, thus rendering the cyclodextrins ineffective as organic residue removing and/or odor controlling actives. Water-soluble preservatives useful in the present invention are those that have a solubility in water of at least about 0.3 g per 100 ml of water, i.e., greater than about 0.3% at room temperature, preferably greater than about 0.5% at room temperature. These types of preservatives have a lower affinity to the cyclodextrin cavity, at least in the aqueous phase, and are therefore more available to provide antimicrobial activity. Preservatives with a water-solubility of less than about 0.3% and a molecular structure that readily fits into the cyclodextrin cavity, have a greater tendency to form inclusion complexes with the cyclodextrin molecules, thus rendering the preservative less effective to control microbes in the cyclodextrin solution. Many well known preservatives such as short chain alkyl esters of p-hydroxybenzoic acid, commonly known as parabens; N-(4-chlorophenyl)-N'-(3,4-dichlorophenyl) urea, also known trichlorocarbanilide or triclocarban, 2,4,4'-trichloro-2'-hydroxy diphenyl ether, commonly known as triclosan are not preferred in the present invention, but can be

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used at levels low enough that an effective amount of cyclodextrin is still available for organic residue removal and/or odor control.

The water-soluble antimicrobial preservative in the present invention is included at an effective amount. The term "effective amount" as herein defined means a level sufficient to prevent spoilage, or prevent growth of inadvertently added microorganisms, for a specific period of time. In other words, the preservative is not necessarily being used to kill microorganisms on the surface onto which the composition is deposited in order to eliminate odors produced by microorganisms. Instead, it is preferably being used to prevent spoilage of the cyclodextrin solution in order to increase the shelf-life of the composition. Preferred levels of preservative are from about 0.0001% to about 0.5%, more preferably from about 0.0002% to about 0.2%, most preferably from about 0.0003% to about 0.1%, by weight of the usage composition.

In order to reserve most of the cyclodextrins for organic residue removal and/or odor control, the cyclodextrin to preservative molar ratio should be greater than about 5:1, preferably greater than about 10:1, more preferably greater than about 50:1, even more preferably greater than about 100:1.

The preservative can be any organic preservative materials which are food compatible, e.g., suitable for direct or indirect food contact use or may be petitioned for food use. Preferred water-soluble preservatives include organic sulfur compounds, halogenated compounds, cyclic organic nitrogen compounds, low molecular weight aldehydes, quaternary ammonium compounds, dehydroacetic acid, phenyl and phenolic compounds, and mixtures thereof.

The following are non-limiting examples of preferred water-soluble preservatives for use in the present invention.

(a). Organic Sulfur Compounds

Preferred water-soluble preservatives for use in the present invention are organic sulfur compounds. Some non-limiting examples of organic sulfur compounds suitable for use in the present invention are:

(i) 3-Isothiazolone Compounds

A preferred preservative is an antimicrobial, organic preservative containing 3-isothiazolone groups having the formula:

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wherein

Y is an unsubstituted alkyl, alkenyl, or alkynyl group of from about 1 to about 18 carbon atoms, an unsubstituted or substituted cycloalkyl group having from about a 3 to about a 6 carbon ring and up to 12 carbon atoms, an unsubstituted or substituted aralkyl group of up to about 10 carbon atoms, or an unsubstituted or substituted aryl group of up to about 10 carbon atoms;

 R^1 is hydrogen, halogen, or a (C_1-C_4) alkyl group; and R^2 is hydrogen, halogen, or a (C_1-C_4) alkyl group.

Preferably, when Y is methyl or ethyl, R¹ and R² should not both be hydrogen. Salts of these compounds formed by reacting the compound with acids such as hydrochloric, nitric, sulfuric, etc. are also suitable.

This class of compounds is disclosed in U.S. Pat. No. 4,265,899, Lewis et al., issued May 5, 1981, and incorporated herein by reference. Examples of said compounds are: 5-chloro-2-methyl-4-isothiazolin-3-one; 2-n-butyl-3-isothiazolone; 2-benzyl-3-isothiazolone; 2-phenyl-3-isothiazolone, 2-methyl-4,5-dichloroisothiazolone; 5-chloro-2-methyl-3-isothiazolone; 2-methyl-4-isothiazolin-3-one; and mixtures thereof. A preferred preservative is a water-soluble mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one, more preferably a mixture of about 77% 5-chloro-2-methyl-4-isothiazolin-3-one and about 23% 2-methyl-4-isothiazolin-3-one, a broad spectrum preservative available as a 1.5% aqueous solution under the trade name Kathon® CG by Rohm and Haas Company.

When Kathon® is used as the preservative in the present invention it is present at a level of from about 0.0001% to about 0.01%, preferably from about 0.0002% to about 0.005%, more preferably from about 0.0003% to about 0.003%, most preferably from about 0.0004% to about 0.002%, by weight of the composition.

Other isothiazolins include 1,2-benzisothiazolin-3-one, available under the trade name Proxel® products; and 2-methyl-4,5-trimethylene-4-isothiazolin-3-one, available under the trade name Promexal®. Both Proxel and Promexal are available from Zeneca. They have stability over a wide pH range (i.e., 4-12). Neither contain active halogen and are not formaldehyde releasing preservatives. Both Proxel and Promexal are effective against typical Gram negative and positive bacteria, fungi and yeasts when used at a level from about 0.001% to about 0.5%, preferably from about 0.005% to about 0.05%, and most preferably from about 0.01% to about 0.02% by weight of the usage composition.

(ii) Sodium Pyrithione

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Another preferred organic sulfur preservative is sodium pyrithione, with water solubility of about 50%. When sodium pyrithione is used as the preservative in the present invention it is typically present at a level of from about 0.0001% to about 0.01%, preferably from about 0.0002% to about 0.005%, more preferably from about 0.0003% to about 0.003%, by weight of the usage composition.

Mixtures of the preferred organic sulfur compounds can also be used as the preservative in the present invention.

(b). Halogenated Compounds

Preferred preservatives for use in the present invention are halogenated compounds. Some non-limiting examples of halogenated compounds suitable for use in the present invention are:

5-bromo-5-nitro-1,3-dioxane, available under the trade name Bronidox L[®] from Henkel. Bronidox L[®] has a solubility of about 0.46% in water. When Bronidox is used as the preservative in the present invention it is typically present at a level of from about 0.0005% to about 0.02%, preferably from about 0.001% to about 0.01%, by weight of the usage composition;

2-bromo-2-nitropropane-1,3-diol, available under the trade name Bronopol® from Inolex can be used as the preservative in the present invention. Bronopol has a solubility of about 25% in water. When Bronopol is used as the preservative in the present invention it is typically present at a level of from about 0.002% to about 0.1%, preferably from about 0.005% to about 0.05%, by weight of the usage composition;

- 1,1'-hexamethylene bis(5-(p-chlorophenyl)biguanide), commonly known as chlorhexidine, and its salts, e.g., with acetic and gluconic acids can be used as a preservative in the present invention. The digluconate salt is highly water-soluble, about 70% in water, and the diacetate salt has a solubility of about 1.8% in water. When chlorohexidine is used as the preservative in the present invention it is typically present at a level of from about 0.0001% to about 0.04%, preferably from about 0.0005% to about 0.01%, by weight of the usage composition.
- 1,1,1-Trichloro-2-methylpropan-2-ol, commonly known as chlorobutanol, with water solubility of about 0.8%; a typical effective level of chlorobutanol is from about 0.1% to about 0.5%, by weight of the usage composition.
- 4,4'- (Trimethylenedioxy)bis-(3-bromobenzamidine) diisethionate, or dibromopropamidine, with water solubility of about 50%, when dibromopropamidine is used as the preservative in the present invention it is typically present at a level of from about 0.0001% to about 0.05%, preferably from about 0.0005% to about 0.01% by weight of the usage composition

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Mixtures of the preferred halogenated compounds can also be used as the preservative in the present invention.

(c). Cyclic Organic Nitrogen Compounds

Preferred water-soluble preservatives for use in the present invention are cyclic organic nitrogen compounds. Some non-limiting examples of cyclic organic nitrogen compounds suitable for use in the present invention are:

(i) Imidazolidinedione Compounds

Preferred preservatives for use in the present invention are imidazolidione compounds. Some non-limiting examples of imidazolidinedione compounds suitable for use in the present invention are:

1,3-bis(hydroxymethyl)-5,5-dimethyl-2,4-imidazolidinedione, commonly known as dimethyloldimethylhydantoin, or DMDM hydantoin, available as, e.g., Glydant® from Lonza. DMDM hydantoin has a water solubility of more than 50% in water, and is mainly effective on bacteria. When DMDM hydantoin is used, it is preferable that it be used in combination with a broad spectrum preservative such as Kathon CG®, or formaldehyde. A preferred mixture is about a 95:5 DMDM hydantoin to 3-butyl-2-iodopropynylcarbamate mixture, available under the trade name Glydant Plus® from Lonza. When Glydant Plus® is used as the preservative in the present invention, it is typically present at a level of from about 0.005% to about 0.2% by weight of the usage composition;

N-[1,3-bis(hydroxymethyl)2,5-dioxo-4-imidazolidinyl]-N,N'-bis(hydroxymethyl) urea, commonly known as diazolidinyl urea, available under the trade name Germall II[®] from Sutton Laboratories, Inc. (Sutton) can be used as the preservative in the present invention. When Germall II[®] is used as the preservative in the present invention, it is typically present at a level of from about 0.01% to about 0.1% by weight of the usage composition;

N,N"-methylenebis{N'-[1-(hydroxymethyl)-2,5-dioxo-4-imidazolidinyl]urea}, commonly known as imidazolidinyl urea, available, e.g., under the trade name Abiol[®] from 3V-Sigma, Unicide U-13[®] from Induchem, Germall 115[®] from (Sutton) can be used as the preservative in the present invention. When imidazolidinyl urea is used as the preservative, it is typically present at a level of from about 0.05% to about 0.2%, by weight of the usage composition.

Mixtures of the preferred imidazolidinedione compounds can also be used as the preservative in the present invention.

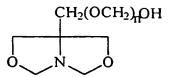
(ii) Polymethoxy Bicyclic Oxazolidine

Another preferred water-soluble cyclic organic nitrogen preservative is polymethoxy bicyclic oxazolidine, having the general formula:

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where n has a value of from about 0 to about 5, and is available under the trade name Nuosept® C from Hüls America. When Nuosept® C is used as the preservative, it is typically present at a level of from about 0.005% to about 0.1%, by weight of the usage composition.

Mixtures of the preferred cyclic organic nitrogen compounds can also be used as the preservative in the present invention.

(d). Low Molecular Weight Aldehydes

(i). Formaldehyde

A preferred preservative for use in the present invention is formaldehyde. Formaldehyde is a broad spectrum preservative which is normally available as formalin which is a 37% aqueous solution of formaldehyde. When formaldehyde is used as the preservative in the present invention, typical levels are from about 0.003% to about 0.2%, preferably from about 0.008% to about 0.1%. more preferably from about 0.01% to about 0.05%, by weight of the usage composition.

(ii) Glutaraldehyde

A preferred preservative for use in the present invention is glutaraldehyde. Glutaraldehyde is a water-soluble, broad spectrum preservative commonly available as a 25% or a 50% solution in water. When glutaraldehyde is used as the preservative in the present invention it is typically present at a level of from about 0.005% to about 0.1%, preferably from about 0.01% to about 0.05%, by weight of the usage composition.

25 (e). **Quaternary Compounds**

Preferred preservatives for use in the present invention are cationic and/or quaternary compounds. Such compounds include polyaminopropyl biguanide, also known as polyhexamethylene biguanide having the general formula:

30 $\text{HCI-NH}_2\text{-(CH}_2)_3\text{-(CII}_2)_3\text{-NH-C(=NII)-NH-C(=NII-IICI)-NH-(CH}_2)_3\text{-(CH}_2)_3\text{-NII-C(=NH)-NH-CN}$

Polyaminopropyl biguanide is a water-soluble, broad spectrum preservative which is available as a 20% aqueous solution available under the trade name

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Cosmocil CQ[®] from ICI Americas, Inc., or under the trade name Mikrokill[®] from Brooks, Inc.

1-(3-Chlorallyl) -3,5,7-triaza-1-azoniaadamantane chloride, available, e.g., under the trade name Dowicil 200 from Dow Chemical, is an effective quaternary ammonium preservative; it is freely soluble in water; however, it has the tendency to discolor (yellow), therefore it is not highly preferred.

Mixtures of the preferred quaternary ammonium compounds can also be used as the preservative in the present invention.

When quaternary ammonium compounds are used as the preservative in the present invention, they are typically present at a level of from about 0.005% to about 0.2%, preferably from about 0.01% to about 0.1%, by weight of the usage composition.

(f). Dehydroacetic Acid

A preferred preservative for use in the present invention is dehydroacetic acid. Dehydroacetic acid is a broad spectrum preservative preferably in the form of a sodium or a potassium salt so that it is water-soluble. This preservative acts more as a biostatic preservative than a biocidal preservative. When dehydroacetic acid is used as the preservative it is typically used at a level of from about 0.005% to about 0.2%, preferably from about 0.008% to about 0.1%, more preferably from about 0.01% to about 0.05%, by weight of the usage composition.

(g). Phenyl and Phenolic Compounds

Some non-limiting examples of phenyl and phenolic compounds suitable for use in the present invention are:

4,4'-diamidino- α,ω -diphenoxypropane diisethionate, commonly known as propamidine isethionate, with water solubility of about 16%; and 4,4'-diamidino- α,ω -diphenoxyhexane diisethionate, commonly known as hexamidine isethionate. Typical effective level of these salts is about 0.0002% to about 0.05% by weight of the usage composition.

Other examples are benzyl alcohol, with a water solubility of about 4%; 2-phenylethanol, with a water solubility of about 2%; and 2-phenoxyethanol, with a water solubility of about 2.67%; typical effective level of these phenyl and phenoxy alcohol is from about 0.1% to about 0.5%, by weight of the usage composition.

(h). Mixtures thereof

(L). ADJUNCT ODOR-CONTROLLING INGREDIENTS

Incorporating adjunct odor-controlling materials can enhance the capacity of the cyclodextrin to control odors as well as broaden the range of odor types and molecule sizes which can be controlled. Such materials include, for example, metallic

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salts, water-soluble cationic and anionic polymers, water-soluble bicarbonate salts, and mixtures thereof.

(a) Water-Soluble Ionic Polymers

Some water-soluble polymers, e.g., water-soluble cationic polymer and water-soluble anionic polymers can be used in the composition of the present invention to provide additional odor control benefits.

(i) Cationic polymers, e.g., polyamines

Water-soluble cationic polymers, e.g., those containing amino functionalities, amido functionalities, and mixtures thereof, are useful in the present invention to control certain acid-type odors.

(ii) Anionic polymers, e.g., polyacrylic acid

Water-soluble anionic polymers, e.g., polyacrylic acids and their water-soluble salts are useful in the present invention to control certain amine-type odors. Preferred polyacrylic acids and their alkali metal salts have an average molecular weight of less than about 20,000, more preferably less than 5,000. Polymers containing sulfonic acid groups, phosphoric acid groups, phosphonic acid groups, and their water-soluble salts, and mixtures thereof, and mixtures with carboxylic acid and carboxylate groups, are also suitable.

Water-soluble polymers containing both cationic and anionic functionalities are also suitable. Examples of these polymers are given in U.S. Pat. 4,909,986, issued March 20, 1990 to N. Kobayashi and A. Kawazoe, incorporated herein by reference. Another example of water-soluble polymers containing both cationic and anionic functionalities is a copolymer of dimethyldiallyl ammonium chloride and acrylic acid, commercially available under the trade name Merquat 280[®] from Calgon.

When a water-soluble polymer is used it is typically present at a level of from about 0.005% to about 5%, preferably from about 0.01% to about 3%, more preferably from about 0.1% to about 2%, by weight of the usage composition.

(b). Soluble Carbonate and/or Bicarbonate Salts

Water-soluble alkali metal carbonate and/or bicarbonate salts, such as sodium bicarbonate, potassium bicarbonate, potassium carbonate, cesium carbonate, sodium carbonate, and mixtures thereof can be added to the composition of the present invention in order to help to control certain acid-type odors, as well as to provide additional sequestrant/builder benefit. Preferred salts are sodium carbonate monohydrate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, and mixtures thereof. When these salts are added to the composition of the present invention, they are typically present at a level of from about 0.1% to about 5%,

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preferably from about 0.2% to about 3%, more preferably from about 0.3% to about 2%, by weight of the composition. When these salts are added to the composition of the present invention it is preferably that incompatible metal salts not be present in the invention. Preferably, when these salts are used the composition should be essentially free of zinc and other incompatible metal ions, e.g., Ca, Fe, Ba, etc. which form water-insoluble salts.

(M). MIXTURES THEREOF OF (B) TO (L); and

(N). CARRIER

Aqueous solutions are preferred for organic residue removal and/or odor control. The dilute aqueous solution provides the maximum separation of cyclodextrin molecules on the food and food contacting surfaces and thereby maximizes the chance that an organic residue, such as a pesticide molecule and/or an odor molecule will interact with a cyclodextrin molecule.

The preferred carrier of the present invention is water. The water which is used can be distilled, deionized, or tap water. Water not only serves as the liquid carrier for the cyclodextrins, but it also facilitates the complexation reaction between the cyclodextrin molecules and any organic residue molecules that are on the food and/or food contacting surfaces when they are treated.

Optionally, in addition to water, the carrier can contain a low molecular weight organic solvent that is highly soluble in water such as ethanol. Low molecular weight alcohols can help to dissolve water insoluble organic residues such as some pesticide and facilitate the complexation and removal of these undesirable materials by cyclodextrin. Low molecular weight alcohols can also help to dissolve the wax that are coated on some food such as apples, and facilitate wax removal by surfactants. The optional water soluble low molecular weight solvent can be used at a level of up to about 50%, typically from about 1% to about 20%, preferably from about 2% to about 15%, more preferably from about 5% to about 10%, by weight of the total composition. Factors that need to consider when a high level of solvent is used in the composition are odor, flammability, and environment impact.

30 (O) OTHER OPTIONAL INGREDIENTS

The composition of the present invention can optionally contain other optional ingredients, such as colorants, antioxidants, and mixtures thereof in addition to the cyclodextrin molecules.

II. ARTICLE OF MANUFACTURE

The composition of the present invention can also be used in an article of manufacture comprising said composition plus a spray dispenser. When the commercial embodiment of the article of manufacture is used, it is optional, but

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preferable, to include the preservative. Therefore, the most basic article of manufacture comprises uncomplexed cyclodextrin, a carrier, and a spray dispenser. Said compositions and/or article of manufacture are preferably in association with instructions to use said compositions and product for cleaning and removal of undesirable materials from food and/or food contacting surfaces.

SPRAY DISPENSER

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The article of manufacture herein comprises a spray dispenser. The food cleaning composition is placed into a spray dispenser in order to be distributed onto the food and/or food contacting surfaces. Said spray dispenser for producing a spray of liquid droplets can be any of the manually activated means as is known in the art, e.g. trigger-type, pump-type, non-aerosol self-pressurized, and aerosol-type spray means, for dispensing the food cleaning composition to a small amount of food and/or food contacting surfaces in consumer's household, such as produce, fruits and vegetables, meat, poultry, fish and other seafoods, food preparing surfaces and/or equipment, such as cutting board, countertop, pots and pans, food containers, and the like, as well as non-manually operated, powered sprayers for conveniently cleaning large amounts of food and/or large areas of food contacting surfaces, e.g., in commercial and/or constitutional settings, such as in supermarkets, restaurants, cafeterias, and the like. The spray dispenser herein can include those that will substantially foam the clear, aqueous food cleaning composition.

The spray dispenser can be an aerosol dispenser. Said aerosol dispenser comprises a container which can be constructed of any of the conventional materials employed in fabricating aerosol containers The dispenser must be capable of withstanding internal pressure in the range of from about 20 to about 110 p.s.i.g., more preferably from about 20 to about 70 p.s.i.g. The one important requirement concerning the dispenser is that it be provided with a valve member which will permit the clear, aqueous food cleaning composition contained in the dispenser to be dispensed in the form of a spray of very fine, or finely divided, particles or droplets. The aerosol dispenser utilizes a pressurized sealed container from which the clear, aqueous food cleaning composition is dispensed through a special actuator/valve assembly under pressure. The aerosol dispenser is pressurized by incorporating therein a gaseous component generally known as a propellant. Common aerosol propellants, e.g., gaseous hydrocarbons such as isobutane, and mixed halogenated hydrocarbons, can be used. Halogenated hydrocarbon propellants such as chlorofluoro hydrocarbons have been alleged to contribute to environmental problems, and are not preferred. When cyclodextrin is present hydrocarbon propellants are not preferred, because they can form complexes with the cyclodextrin

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molecules thereby reducing the availability of uncomplexed cyclodextrin molecules for absorption of unwanted odor and other organic residue materials. Preferred propellants are compressed air, nitrogen, inert gases, carbon dioxide, etc. A more complete description of commercially available aerosol-spray dispensers appears in U.S. Pat. Nos.: 3,436,772, Stebbins, issued April 8, 1969; and 3,600,325, Kaufman et al., issued August 17, 1971; both of said references are incorporated herein by reference.

Preferably the spray dispenser can be a self-pressurized non-aerosol container having a convoluted liner and an elastomeric sleeve. Said self-pressurized dispenser comprises a liner/sleeve assembly containing a thin, flexible radially expandable convoluted plastic liner of from about 0.010 to about 0.020 inch thick, inside an essentially cylindrical elastomeric sleeve. The liner/sleeve is capable of holding a substantial quantity of food cleaning composition product and of causing said product to be dispensed. A more complete description of self-pressurized spray dispensers can be found in U.S. Pat. Nos. 5,111,971, Winer, issued May 12, 1992, and 5,232,126, Winer, issued Aug. 3, 1993; both of said references are herein incorporated by reference. Another type of aerosol spray dispenser is one wherein a barrier separates the food cleaning composition from the propellant (preferably compressed air or nitrogen), as disclosed in U.S. Pat. No. 4,260,110, issued April 7, 1981, and incorporated herein by reference. Such a dispenser is available from EP Spray Systems, East Hanover, New Jersey.

More preferably, the spray dispenser is a non-aerosol, manually activated, pump-spray dispenser. Said pump-spray dispenser comprises a container and a pump mechanism which securely screws or snaps onto the container. The container comprises a vessel for containing the aqueous food cleaning composition to be dispensed.

The pump mechanism comprises a pump chamber of substantially fixed volume, having an opening at the inner end thereof. Within the pump chamber is located a pump stem having a piston on the end thereof disposed for reciprocal motion in the pump chamber. The pump stem has a passageway there through with a dispensing outlet at the outer end of the passageway and an axial inlet port located inwardly thereof.

The container and the pump mechanism can be constructed of any conventional material employed in fabricating pump-spray dispensers, including, but not limited to: polyethylene; polypropylene; polyethyleneterephthalate; blends of polyethylene, vinyl acetate, and rubber elastomer. A preferred container is made of clear, e.g., polyethylene terephthalate. Other materials can include stainless steel. A

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more complete disclosure of commercially available dispensing devices appears in: U.S. Pat. Nos.: 4,895,279, Schultz, issued January 23, 1990; 4,735,347, Schultz et al., issued April 5, 1988; and 4,274,560, Carter, issued June 23, 1981; all of said references are herein incorporated by reference.

Most preferably, the spray dispenser is a manually activated trigger-spray dispenser. Said trigger-spray dispenser comprises a container and a trigger both of which can be constructed of any of the conventional material employed in fabricating trigger-spray dispensers, including, but not limited to: polyethylene; polypropylene; polyacetal; polycarbonate; polyethyleneterephthalate; polyvinyl chloride; polystyrene; blends of polyethylene, vinyl acetate, and rubber elastomer. Other materials can include stainless steel and glass. A preferred container is made of clear, e.g. polyethylene terephthalate. The trigger-spray dispenser does not incorporate a propellant gas into the food cleaning composition, and preferably it does not include those that will foam the food cleaning composition. The trigger-spray dispenser herein is typically one which acts upon a discrete amount of the food cleaning composition itself, typically by means of a piston or a collapsing bellows that displaces the composition through a nozzle to create a spray of thin liquid. Said trigger-spray dispenser typically comprises a pump chamber having either a piston or bellows which is movable through a limited stroke response to the trigger for varying the volume of said pump chamber. This pump chamber or bellows chamber collects and holds the product for dispensing. The trigger spray dispenser typically has an outlet check valve for blocking communication and flow of fluid through the nozzle and is responsive to the pressure inside the chamber. For the piston type trigger sprayers, as the trigger is compressed, it acts on the fluid in the chamber and the spring, increasing the pressure on the fluid. For the bellows spray dispenser, as the bellows is compressed, the pressure increases on the fluid. The increase in fluid pressure in either trigger spray dispenser acts to open the top outlet check valve. The top valve allows the product to be forced through the swirl chamber and out the nozzle to form a discharge pattern. An adjustable nozzle cap can be used to vary the pattern of the fluid dispensed.

For the piston spray dispenser, as the trigger is released, the spring acts on the piston to return it to its original position. For the bellows spray dispenser, the bellows acts as the spring to return to its original position. This action causes a vacuum in the chamber. The responding fluid acts to close the outlet valve while opening the inlet valve drawing product up to the chamber from the reservoir.

A more complete disclosure of commercially available dispensing devices appears in U.S. Pat. Nos. 4,082,223, Nozawa, issued Apr. 4, 1978; 4,161, 288,

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McKinney, issued Jul. 17, 1985; 4,434,917, Saito et al., issued Mar. 6, 1984; and 4,819,835, Tasaki, issued Apr. 11, 1989; 5,303,867, Peterson, issued Apr. 19, 1994; all of said references are incorporated herein by reference.

A broad array of trigger sprayers or finger pump sprayers are suitable for use with the compositions of this invention. These are readily available from suppliers such as Calmar, Inc., City of Industry, California, CSI (Continental Sprayers, Inc.), St. Peters, Missouri, Berry Plastics Corp., Evansville, Indiana, a distributor of Guala sprayers; or Seaquest Dispensing, Cary, Illinois.

The preferred trigger sprayers are the blue inserted Guala sprayer, available from Berry Plastics Corp., or the Calmar TS800-1A, TS1300, and TS-800-2, available from Calmar Inc., because of the fine uniform spray characteristics, spray volume, and pattern size. More preferred are sprayers with precompression features and finer spray characteristics and even distribution, such as Yoshino sprayers from Japan. Any suitable bottle or container can be used with the trigger sprayer, the preferred bottle is a 17 fl-oz. bottle (about 500 ml) of good ergonomics similar in shape to the Cinch bottle. It can be made of any materials such as high density polyethylene, polypropylene, polyvinyl chloride, polystyrene, polyethylene terephthalate, glass, or any other material that forms bottles. Preferably, it is made of high density polyethylene or clear polyethylene terephthalate.

For smaller fluid ounce sizes (such as 1 to 8 ounces), a finger pump can be used with canister or cylindrical bottle. The preferred pump for this application is the cylindrical Euromist II[®] from Seaquest Dispensing. More preferred are those with precompression features.

The article of manufacture herein can also comprise a non-manually operated spray dispenser. By "non-manually operated" it is meant that the spray dispenser can be manually activated, but the force required to dispense the food cleaning composition is provided by another, non-manual means. Non-manually operated sprayers include, but are not limited to, powered sprayers, air aspirated sprayers, liquid aspirated sprayers, electrostatic sprayers, and nebulizer sprayers. The food cleaning composition is placed into a spray dispenser in order to be distributed onto the food and/or food contacting surfaces. The non-manually operated spray dispensers are particularly useful to wash and clean a large amount of food and/or a large area of food contacting surfaces, such as in commercial and/or constitutional settings, e.g., in supermarkets, restaurants, cafeterias, and the like

Powered sprayers include self contained powered pumps that pressurize the aqueous food cleaning composition and dispense it through a nozzle to produce a spray of liquid droplets. Powered sprayers are attached directly or remotely through

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the use of piping/tubing to a reservoir (such as a bottle) to hold the aqueous food cleaning composition. Powered sprayers may include, but are not limited to, centrifugal or positive displacement designs. It is preferred that the powered sprayer be powered by a portable DC electrical current from either disposable batteries (such as commercially available alkaline batteries) or rechargeable battery units (such as commercially available nickel cadmium battery units). Powered sprayers may also be powered by standard AC power supply available in most buildings. The discharge nozzle design can be varied to create specific spray characteristics (such as spray diameter and particle size). It is also possible to have multiple spray nozzles for different spray characteristics. The nozzle can comprise an adjustable nozzle shroud that would allow the spray characteristics to be altered.

Nonlimiting examples of commercially available powered sprayers are disclosed in U.S. Pat. Nos. 4,865,255, Luvisotto, issued Sep. 12, 1989 which is incorporated herein by reference. Preferred powered sprayers are readily available from suppliers such as Solo, Newport News, Virginia (e.g., Solo Spraystar TM rechargeable sprayer, listed as manual part #: US 460.395) and Multi-sprayer Systems, Minneapolis, Minnesota (e.g., model: Spray 1).

Air aspirated sprayers include the classification of sprayers generically known as "air brushes". A stream of pressurized air draws up the aqueous food cleaning composition and dispenses it through a nozzle to create a spray of liquid. The food cleaning composition can be supplied via separate piping/tubing or more commonly is contained in a jar to which the aspirating sprayer is attached.

Nonlimiting examples of commercially available air aspirated sprayers appears in U.S. Pat. Nos. 1,536,352, Murray, issued Apr. 22, 1924 and 4,221,339, Yoshikawa, issues Sep. 9, 1980; all of said references are incorporated herein by reference. Air aspirated sprayers are readily available from suppliers such as The Badger Air-Brush Co., Franklin Park, Illinois (e.g., model #: 155) and Wilton Air Brush Equipment, Woodridge, Illinois (e.g., stock #: 415-4000, 415-4001, 415-4100).

Liquid aspirated sprayers are typical of the variety in widespread use to spray garden chemicals. The aqueous food cleaning composition is drawn into a fluid stream by means of suction created by a Venturi effect. The high turbulence serves to mix the aqueous food cleaning composition with the fluid stream (typically water) in order to provide a uniform mixture/concentration. It is possible with this method of delivery to dispense the aqueous concentrated food cleaning composition of the present invention and then dilute it to a selected concentration with the delivery stream.

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DESCRIPTION OF SERVICE 1 1 3

Liquid aspirated sprayers are readily available from suppliers such as Chapin Manufacturing Works, Batavia, New York (e.g., model #: 6006).

Electrostatic sprayers impart energy to the aqueous food cleaning composition via a high electrical potential. This energy serves to atomize and charge the aqueous food cleaning composition, creating a spray of fine, charged particles. As the charged particles are carried away from the sprayer, their common charge causes them to repel one another. This has two effects before the spray reaches the target. First, it expands the total spray mist. This is especially important when spraying to fairly distant, large areas. The second effect is maintenance of original particle size. Because the particles repel one another, they resist collecting together into large, heavier particles like uncharged particles do. This lessens gravity's influence, and increases the charged particle reaching the target. As the mass of negatively charged particles approach the target, they push electrons inside the target inwardly, leaving all the exposed surfaces of the target with a temporary positive charge. The resulting attraction between the particles and the target overrides the influences of gravity and inertia. As each particle deposits on the target, that spot on the target becomes neutralized and no longer attractive. Therefore, the next free particle is attracted to the spot immediately adjacent and the sequence continues until the entire surface of the target is covered. Hence, charged particles improve distribution and reduce drippage.

Nonlimiting examples of commercially available electrostatic sprayers appears in U.S. Pat. Nos. 5,222,664, Noakes, issued Jun. 29, 1993; 4,962,885, Coffee, issued Oct. 16, 1990; 2,695,002, Miller, issued Nov. 1954; 5,405,090, Greene, issued Apr. 11, 1995; 4,752,034, Kuhn, issued Jun. 21, 1988; 2,989,241, Badger, issued Jun. 1961; all of said patents are incorporated herein by reference. Electrostatic sprayers are readily available from suppliers such as Tae In Tech Co, South Korea and Spectrum, Houston, Texas.

Nebulizer sprayers impart energy to the aqueous food cleaning composition via ultrasonic energy supplied via a transducer. This energy results in the aqueous food cleaning composition to be atomized. Various types of nebulizers include, but are not limited to, heated, ultrasonic, gas, venturi, and refillable nebulizers.

Nonlimiting examples of commercially available nebulizer sprayers appears in U.S. Pat. Nos. 3,901,443, Mitsui, issued Aug. 26, 1975; 2,847,248, Schmitt, issued Aug. 1958; 5,511,726, Greenspan, issued Apr. 30, 1996; all of said patents are incorporated herein by reference. Nebulizer sprayers are readily available from suppliers such as A&D Engineering, Inc., Milpitas, California (e.g., model A&D Un-

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231 ultrasonic handy nebulizer) and Amici, Inc., Spring City, Pennsylvania (model: swirler nebulizer).

The preferred article of manufacture herein comprises a non-manually operated sprayer, such as a battery-powered sprayer, containing the aqueous food cleaning composition. More preferably the article of manufacture comprises a combination of a non-manually operated sprayer and a separate container of the aqueous food cleaning composition, to be added to the sprayer before use and/or to be separated for filling/refilling. The separate container can contain a usage composition, or a concentrated composition to be diluted before use, and/or to be used with a diluting sprayer, such as with a liquid aspirated sprayer, as described herein above.

Also, as described hereinbefore, the separate container should have structure that mates with the rest of the sprayer to ensure a solid fit without leakage, even after motion, impact, etc. and when handled by inexperienced consumers. The sprayer desirably can also have an attachment system that is safe and preferably designed to allow for the liquid container to be replaced by another container that is filled. E.g., the fluid reservoir can be replaced by a filled container. This can minimize problems with filling, including minimizing leakage, if the proper mating and sealing means are present on both the sprayer and the container. Desirably, the sprayer can contain a shroud to ensure proper alignment and/or to permit the use of thinner walls on the replacement container. This minimizes the amount of material to be recycled and/or discarded. The package sealing or mating system can be a threaded closure (sprayer) which replaces the existing closure on the filled and threaded container. A gasket is desirably added to provide additional seal security and minimize leakage. The gasket can be broken by action of the sprayer closure. These threaded sealing systems can be based on industry standards. However, it is highly desirable to use a threaded sealing system that has non-standard dimensions to ensure that the proper sprayer/bottle combination is always used. This helps prevent the use of fluids that are toxic, which could then be dispensed when the sprayer is used for its intended purpose.

An alternative sealing system can be based on one or more interlocking lugs and channels. Such systems are commonly referred to as "bayonet" systems. Such systems can be made in a variety of configurations, thus better ensuring that the proper replacement fluid is used. For convenience, the locking system can also be one that enables the provision of a "child-proof" cap on the refill bottle. This "lock-and-key" type of system thus provides highly desirable safety features. There are a variety of ways to design such lock and key sealing systems.

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Care must be taken, however, to prevent the system from making the filling and sealing operation too difficult. If desired, the lock and key can be integral to the sealing mechanism. However, for the purpose of ensuring that the correct recharge or refill is used, the interlocking pieces can be separate from the sealing system. E.g., the shroud and the container could be designed for compatibility. In this way, the unique design of the container alone could provide the requisite assurance that the proper recharge/refill is used.

Examples of threaded closures and bayonet systems can be found in U.S. Pat. 4,781,311, Nov. 1, 1988 (Angular Positioned Trigger Sprayer with Selective Snap-Screw Container Connection, Clorox), U.S. Pat. 5,560,505, Oct. 1, 1996 (Container and Stopper Assembly Locked Together by Relative Rotation and Use Thereof, Cebal SA), and U.S. Pat. 5,725,132, Mar. 10, 1998 (Dispenser with Snap-Fit Container Connection, Centico International). All of said patents are incorporated herein by reference.

III. METHOD OF USE

The present invention also relates to methods for removing dirt and other unwanted residues from food, food products, food preparation surfaces and/or food contact surfaces, and to detersive compositions, especially in liquid form, preferably clear compositions, which are especially suitable for practicing said methods.

In-use, the compositions of the present invention typically are applied, e.g., through a trigger-type spray device, directly to soiled food and/or food contact surfaces, optionally with different degree of scrubbing as may be required, and subsequently rinsed off with water. For instance, fruits and vegetables such as apples, grapes, peaches, potatoes, lettuce, tomatoes, celery, and the like, are sprayed with the liquid compositions of the present invention in a spray device, with light scrubbing as may be required. After rinsing in tap water, the fruits and vegetables are cleaner and/or have less organic chemical residues, and are ready for use. Similarly, edible protein food such as meat, poultry, fish and other seafood are sprayed with the compositions of the present invention, slightly scrubbed as needed, and rinsed with tap water to yield foods which are fresher, less odorous and/or less contaminated with microorganisms. In the same manner, a cutting board that is used to cut, e.g., fish, seafood, onion, garlic, or other odorous foods, is sprayed with the clear liquid composition of the present invention and scrubbed then rinsed with tap water becomes clean and absent of undesirable smell.

For use during production of produce, the compositions are typically applied by either a non-manually operated powered spray dispenser, or as dilute solutions in which the produce is dipped. The produce is then rinsed to remove the undesirable

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materials. This method is highly desirable for treatment of any produce that is then sealed, e.g., by application of a, e.g., wax, coating. The current coating used on apples seals in any pesticide residue on the apple and makes it more difficult to remove. The present method improves removal of such pesticides by making them easier to remove. Since pesticides are applied while the produce is still in the field, more complete removal when the produce is picked will improve the produce for the final consumer. Some other actives such as some fungicides and sprouting inhibitors and growth regulators are treated after harvest and before packaging, it is desirable to remove them at the point of consumption, e.g., in the consumer's home or at the food preparation areas of restaurants and cafeterias.

Such large scale cleaning which uses a non-manually operated sprayer to dispense the compositions of the present invention is also very useful for commercial and/or institutional food serving facilities such as restaurants and cafeterias to clean a large amount of fresh fruits and vegetables to serve customers with cleaner and safer food.

The cyclodextrin solution, which contains, e.g., surfactant and/or antimicrobial compound, etc., can be used by distributing, e.g., by placing the aqueous solution into a dispensing means, preferably a spray dispenser and spraying an effective amount onto the desired food and/or food contacting surface for cleaning. An effective amount, as defined herein, means an amount sufficient to remove soils and absorb unwanted materials to the point that consumption by humans is safer and/or more desirable. Distribution can be achieved by using a spray device, a roller, a pad, etc. Soils and other unwanted organic residues can also be removed by dipping the food products or equipment into a bath of the compositions of the present invention.

The present invention also encompasses the method of spraying an effective amount of cyclodextrin solution onto food preparation surfaces such as countertops, cutting boards, and food containers.

The present invention relates to the method of spraying a mist of an effective amount of cyclodextrin solution into and/or onto major household appliances including, but not limited to: refrigerators, freezers, ovens, microwave ovens, dishwashers etc., to remove unwanted residues and/or malodor. Unwanted residues can result when, e.g., one sprays the area with consumer products containing chemicals to kill bugs.

The presence of the surfactant promotes spreading of the solution and the antimicrobial active provides improved odor control as well as antimicrobial action, by minimizing the formation of odors. Both the surfactant and the antimicrobial

active provide improved performance and the mixture is especially effective. When the compositions are applied in the form of the very small particles, as disclosed hereinbefore, additional benefits are found, since the distribution is even further improved and overall performance is improved.

All percentages, ratios, and parts herein, in the Specification, Examples, and Claims are by weight and are approximations unless otherwise stated. All patents and publications herein are incorporated herein, at least in the relevant portions, by reference.

The following are non-limiting examples of the instant composition. Perfume compositions that are used herein are as follows:

Perfume A - Citrus Odor

Perfume Ingredients	Wt.%
Allyl amyl glycolate	1.00
Allyl caproate	2.00
alpha Pinene	4.00
beta Pinene	2.50
Camphor gum	1.30
cis Jasmone	0.20
Citral	9.80
Cyclal c	0.40
Decyl aldehyde	2.00
Dihydro myrcenol	4.50
Fructone	4.60
Geraniol	4.00
Geranyl nitrile	1.50
Hydroxycitronellal	2.00
Iso bornyl acetate	4.60
Iso cyclo citral	8.50
Iso jasmone	0.40
Laevo carvone	0.60
Linalool	7.00
Lyral	6.50
Methyl anthranilate	3.00
Methyl beta-naphthyl ketone	5.00
Methyl dihydro jasmonate	12.00
Methyl heptenone	0.30
Methyl iso butenyl tetrahydro pyran	0.50
Octyl alcohol	1.00
Orange terpenes	3.00
Phenyl ethyl alcohol	2.10
Terpineol	5.00
Vanillin	0.70
Total	100.00

Perfume B - Peach Odor

Perfume Ingredients Wt.%

2 - Methyl butyric acid	1.00
Benzyl acetate	10.00
Cis-3 hexenol 10% DPG	2.00
Cis-3-hexenyl formate	0.50
Damascenone	0.50
Delta decalactone	5.50
delta Nonalactone	2.00
delta Octalactone	2.00
Dimethyl benzyl carbinol	5.00
Dimethyl benzyl carbinyl butyrate	10.00
Ethyl caproate	1.50
gamma Decalactone	0.00
gamma Dodecen-6-lactone	1.00
Geraniol	15.00
Geranyl acetate	2.00
Linalool	30.00
Linalool oxide	2.00
Methyl anthranilate	3.00
Methyl dihydro jasmonate	0.50
Methyl eugenol	6.00
Vanillin	0.50
Total	100.00

Perfume C - Pineapple Odor

<u>Pertume Ingredients</u>	Wt. %
Acetate tcd (conffirm)	0.50
Allyl amyl glycolate	2.00
Allyl caproate	4.00
Anisic aldehyde	1.00
Benzyl acetate	2.00
Benzyl propionate	3.00
beta gamma Hexenol	0.40
Cinnamic alcohol	2.00
Cis jasmone	0.30
Dimethyl benzyl carbinyl acetate	3.00
Ethyl acetoacetate	5.00
Ethyl butyrate	1.00
Ethyl phenyl acetate	3.00
Ethyl vanillin	0.10
Flor acetate	9.60
Fructone	28.00
Frutene	6.00
Geraniol	3.00
Heliotropin	2.00
Hydroxycitronellal	1.00
Indol	0.10
Linalool	5.00
Methyl anthranilate	10.00

DESCRIPTION OF THE PROPERTY I

Para hydroxy phenyl butanone	1.00
Phenyl ethyl alcohol	7.00
	100.00

Perfume D - Raspberry Odor

Perfume Ingredients	Wt.%
2- Methyl pentanoic acid	1.20
Amyl acetate	4.00
Benzyl acetate	37.10
Cis 3 hexenyl acetate	0.80
Cis-3-hexenol	0.80
Citral	1.00
Coumarin	1.00
delta Decalactone	1.20
Dimethyl anthranilate	0.80
Dimethyl benzyl carbinol	1.90
Ethyl acetate	2.00
Ethyl butyrate	4.00
Ethyl caproate	0.80
Ethyl methyl phenyl glycidate	6.40
Ethyl methyl butyrate	2.00
Ethyl vanillin	0.10
Hydroquinone dimethyl ether	1.00
Iso eugenol	1.00
Linalool	20.00
Menthone racemic	0.70
Methyl anthranilate	4.00
Methyl heptenone	0.10
Nonalactone	2.00
Para cresyl methyl ether	0.10
Para hydroxy phenyl butanone	4.00
Undecavertol	0.80
Vanillin	1.20
Total	100.00

Perfume E - Strawberry Odor

Perfume Ingredients	Wt.%
Benzyl acetate	2.00
Benzyl alcohol	54.50
Cinnamic alcohol	1.00
Cinnamic aldehyde	0.30
Cis 3 hexenol	3.00
Cis 3 hexenyl formate	0.10
Citral	1.00
delta Decalactone	1.00
Ethyl acetate	2.50
Ethyl acetoacetate	2.50

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Ethyl butyrate	15.00
Ethyl maltol	1.00
Ethyl methyl butyrate	4.50
Ethyl methyl phenyl glycidate	1.00
Ethyl propyl ketone	4.00
Geranyl acetate	1.50
Maltol isobutyrate	0.50
Methyl cinnamate	3.00
Methyl heptenone	0.10
Vanillin	1.50
Tota	1 100.00

The following are non-limiting examples of the instant composition. The following compositions are prepared by mixing and dissolving the ingredients in waterto form clear solutions.

Ingredients Wt% Description Percent the control of t	Examples	Ţ	<u>11</u>	<u>111</u>	<u>1V</u>	$\underline{\mathbf{V}}$
HPBCD(a) 1.0 1.5 1.5	<u>Ingredients</u>	<u>Wt%</u>	<u>Wt%</u>	<u>Wt%</u>	<u>Wt%</u>	<u>Wt%</u>
Silwet 7600 1.0 1.5 1.5 Pluronic L64 0.8 1.5 Pluronic L61 0.1 0.1 Chlorhexidine 0.03 0.05 ZnCl2 0.05 Perfume A 0.005 Perfume B 0.01 Perfume C 0.05 Perfume D 0.05 Perfume E 0.01 Proxel(b) 0.005 0.01 Kathon 3 ppm 3 ppm Methyl paraben 0.06 0.1 Propylene glycol 0.06 0.1 HCl to pH 5 to pH 5 to pH 5 to pH 5	beta-Cyclodextrin	1.0	1.2			
Pluronic L64 0.8 1.5 Pluronic L61 0.1 0.1 Chlorhexidine 0.03 0.05 ZnCl2 1.0 Perfume A 0.005 Perfume B 0.01 Perfume C 0.05 Perfume D 0.05 0.08 0.08 0.08 0.08	HPBCD(a)			1.2	2.0	1.5
Pluronic L61 0.1 0.1 Chlorhexidine 0.03 0.05 ZnCl2 1.0 Perfume A 0.005 Perfume B 0.01 Perfume C 0.05 Perfume D 0.05 Perfume E 0.01 0.08 Proxel(b) 0.005 0.01 0.08 Proxel(b) 0.005 0.01 3 ppm 3 ppm 3 ppm 0.01	Silwet 7600	1.0			1.5	1.5
Chlorhexidine 0.03 0.05 ZnCl2 1.0 Perfume A 0.005 Perfume B 0.01 Perfume C 0.05 Perfume D 0.05 Perfume E 0.05 0.08 Proxel(b) 0.005 0.01 0.08 Proxel(b) 0.005 0.01 3 ppm Methyl paraben 0.06 0.1 Propylene glycol 0.06 0.1 Ethanol 3.0 5.0 3.0 HCl to pH 5	Pluronic L64		0.8	1.5		
ZnCl2 1.0 Perfume A 0.005 Perfume B 0.01 Perfume C 0.05 Perfume D 0.05 Perfume E 0.05 Proxel(b) 0.005 0.01 Kathon 3 ppm 3 ppm Methyl paraben 0.06 0.1 Propylene glycol 0.06 0.1 Ethanol 3.0 5.0 3.0 HCl to pH 5	Pluronic L61		0.1		0.1	
Perfume A 0.005	Chlorhexidine	0.03			0.05	
Perfume B 0.01 Perfume C 0.05 Perfume D 0.05 Perfume E 0.08 Proxel(b) 0.005 0.01 Kathon 3 ppm 3 ppm Methyl paraben 0.01 Propylene glycol 0.06 0.1 Ethanol 3.0 5.0 3.0 HCl to pH 5	ZnCl ₂					1.0
Perfume C 0.05 Perfume D 0.05 Perfume E 0.08 Proxel(b) 0.005 0.01 Kathon 3 ppm 3 ppm Methyl paraben 0.01 Propylene glycol 0.06 0.1 Ethanol 3.0 5.0 3.0 HCl to pH 5	Perfume A	0.005				
Perfume D 0.05 Perfume E 0.08 Proxel(b) 0.005 0.01 Kathon 3 ppm 3 ppm Methyl paraben 0.01 Propylene glycol 0.06 0.1 Ethanol 3.0 5.0 3.0 HCl to pH 5	Perfume B		0.01			
Perfume E 0.08 Proxel(b) 0.005 0.01 Kathon 3 ppm 3 ppm Methyl paraben 0.01 Propylene glycol 0.06 0.1 Ethanol 3.0 5.0 3.0 HCl to pH 5	Perfume C			0.05		
Proxel(b) 0.005 0.01 Kathon 3 ppm 3 ppm Methyl paraben 0.01 Propylene glycol 0.06 0.1 Ethanol 3.0 5.0 3.0 HCl to pH 5	Perfume D				0.05	
Kathon 3 ppm 3 ppm Methyl paraben 0.01 Propylene glycol 0.06 0.1 Ethanol 3.0 5.0 3.0 HCl to pH 5						0.08
Methyl paraben 0.01 Propylene glycol 0.06 0.1 Ethanol 3.0 5.0 3.0 HCl to pH 5	Proxel(b)	0.005		0.01		
Propylene glycol 0.06 0.1 Ethanol 3.0 5.0 3.0 HCl to pH 5 to pH 5 to pH 5 to pH 5 to pH 4	Kathon		3 ppm			3 ppm
Ethanol 3.0 5.0 3.0 HCl to pH 5 to pH 5 to pH 5 to pH 5	Methyl paraben				0.01	
HCl to pH 5 to pH 5 to pH 5 to pH 4	Propylene glycol			0.06	0.1	
	Ethanol	3.0	5.0	3.0		
Distilled water Bal. Bal. Bal. Bal. Bal.	HCl	to pH 5	to pH 5	to pH 5	to pH 5	to pH 4
	Distilled water	Bal.	Bal.	Bal.	Bal.	Bal.

⁽a) Hydroxypropyl beta-cyclodextrin.

⁽b) 1,2-Benzisothiazolin-3-one.

Examples	<u>VI</u>	<u>VII</u>	<u>viii</u>	<u>IX</u>	<u>X</u>
<u>Ingredients</u>	Wt%	Wt%	Wt%	Wt%	Wt%
beta-Cyclodextrin	1.0	1.0			
beta-Cyclodextrin HPBCD(a)	. 		1.2	2.0	2.0
Pluronic L64		0.5	1.5		
Pluronic L61					0.1

Silwet 7600	0.5			1.0	1.0
Chlorhexidine			0.05		
Bardac 2050(b)				0.03	
ZnCl ₂	0.2				
Sodium bicarbonate				2.0	
Polyacrylic acid(c)					0.1
Perfume D	0.005				,
Perfume E		0.01			
Perfume A			0.05		
Perfume B				0.05	
Perfume C					0.05
Kathon	3 ppm				
Promexal(d)		0.003		*	
Proxel(e)			0.005		
Methyl paraben				0.005	0.005
Propylene glycol			0.06	0.1	
DC-4270(f)				0.1	
Ethanol	3.0	5.0	3.0		
HCI	to pH 4	to pH 5	to pH 4		
NaOH					to pH 9
Distilled water	Bal.	Bal.	Bal.	Bal.	Bal.

- (a) Hydroxypropyl beta-cyclodextrin.
- (b) Dioctyl dimethyl ammonium chloride, 50% solution.
- (c) Polyacrylic acid, average MW about 2,500.
- (d) 2-Methyl-4,5-trimethylene-4-isothiazolin-3-one.
- 5 (e) 1,2-Benzisothiazolin-3-one.

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(f) Silicone suds suppressor available from Dow Corning

The compositions of the above Examples are sprayed onto soiled produce, e.g., fruits and vegetables such as apples, grapes, peaches, potatoes, lettuce, tomatoes, celery, and the like, using a blue inserted Guala® trigger sprayer, available from Berry Plastics Corp., with light scrubbing as may be required. The produce is then rinsed in tap water to remove the unwanted materials.

The compositions of the above Examples are sprayed onto protein foods such as defrost meat, stored fish and seafood, and the like, that have developed some off odor, using a cylindrical Euromist II® pump sprayer available from Seaquest Dispensing, with light scrubbing as may be required. They are then rinsed in tap water to obtain fresher foods with low off odor.

The compositions of Examples I, IV, VIII, and IX are sprayed onto large stainless steel trays that previously are used to marinate chicken quarters, using a rechargeable battery-operated Solo Spraystar sprayer, with scrubbing as may be required. The treated trays are then rinsed off in tap water with scrubbing as may be required, let dry, and are ready to be reused.

WHAT IS CLAIMED IS:

- 1. A food cleaning composition comprising:
- A. an effective amount to absorb unwanted organic molecules of solubilized, uncomplexed cyclodextrin, optionally either a beta-cyclodextrin; b. methylated beta-cyclodextrin; c. a mixture of methylated alpha-cyclodextrin and methylated beta-cyclodextrin; d. hydroxypropyl beta-cyclodextrin; e. mixture of hydroxypropyl alpha-cyclodextrin and hydroxypropyl beta-cyclodextrin; f. selected from the group consisting of beta-cyclodextrin, alpha-cyclodextrin, gamma-cyclodextrin, derivatives of said cyclodextrins, and mixtures thereof, said derivatives optionally being selected from the group consisting of methyl substituted cyclodextrins, ethyl substituted cyclodextrins, hydroxyalkyl substituted cyclodextrins, branched cyclodextrins, cationic cyclodextrins, quaternary ammonium cyclodextrins, anionic cyclodextrins, amphoteric cyclodextrins, cyclodextrins wherein at least one glucopyranose unit has a 3-6-anhydro-cyclomalto structure; or g. mixtures thereof;
- B. optionally, an effective amount to improve the performance of the composition, of cyclodextrin compatible surfactant;
 - C. optionally, an effective amount, to kill, or reduce the growth of microorganisms, of cyclodextrin compatible and water soluble antimicrobial active;
 - D. optionally, an effective amount of sequestrant/builder to improve cleaning;
- E. optionally, an effective amount to improve acceptance of the composition of hydrophilic perfume containing at least about 50% by weight of the perfume of ingredients having a ClogP of less than about 3.5 and, optionally, a minor amount of perfume ingredients selected from the group consisting of ambrox, bacdanol, benzyl salicylate, butyl anthranilate, cetalox, damascenone, alphadamascone, gamma-dodecalactone, ebanol, herbavert, cis-3-hexenyl salicylate, alphadionone, beta-ionone, alpha-isomethylionone, lilial, methyl nonyl ketone, gamma-undecalactone, undecylenic aldehyde, and mixtures thereof;
- F. optionally, from about 0.01% to about 3% by weight of the composition of low molecular weight polyol;
- G. optionally, from about 0.001% to about 0.3% by weight of the composition of aminocarboxylate chelator;
- H. optionally, an effective amount to reduce foaming, of antifoaming agent;

- I. optionally, an effective amount of metallic salt for improved odor benefit;
- J. optionally, an effective amount of enzyme for improved cleaning and odor control benefit;
- K. optionally, an effective amount of solubilized, water-soluble, antimicrobial preservative;
- L. optionally, an effective amount of adjunct odor-controlling ingredients selected from the group consisting of alkali carbonate and bicarbonate salts, low molecular weight water soluble ionic polymers, and mixtures thereof; and
- M. aqueous carrier, said composition containing at least one of (B) and (C), and containing, essentially, only ingredients which are food compatible, and/or preferably having a pH of more than about 3, more preferably more than about 3.5, said composition optionally being packaged in a container that is capable of dispensing said composition as either 1) small droplets having a weight average diameter of from about 10 μm to about 120 μm. and/or 2) a foam, said container optionally being part of an article of manufacture which also comprises non-manually operated spray means, and/or said composition being packaged in association with instructions to use it to clean and/or deodorize food and/or food contact surfaces.
- 2. The composition of Claim 1 wherein either a. said cyclodextrin is present at a level of from about 0.01% to about 20% by weight of the composition and said surfactant is present at a level of from about 0.01% to about 15% by weight of the composition; b. said cyclodextrin is present at a level of from about 0.01% to about 5% by weight of the composition and said surfactant is present at a level of from about 0.03% to about 4% by weight of the composition; c. said cyclodextrin is present at a level of from about 0.1% to about 3%, by weight of the composition and said surfactant is present at a level of from about 0.05% to about 3% by weight of the composition; or d. said cyclodextrin is present at a level of from about 0.5% to about 2%, by weight of the composition and said surfactant is present at a level of from about 0.1% to about 2% by weight of the composition.
- 3. The composition of Claim 1 or Claim 2 wherein said surfactant is present in an effective amount, optionally to provide a surface tension of from about 20 dyne/cm to about 45 dyne/cm, and is optionally selected from the group consisting of: block copolymers of ethylene oxide and propylene oxide, optionally a block copolymer of ethylene oxide and propylene oxide based on ethylene glycol, propylene glycol,

glycerol, trimethylolpropane, ethylenediamine, or mixtures thereof as the initial reactive hydrogen compound, or surfactant which has the general formula $H(EO)_n(PO)_m(EO)_nH$, wherein EO is an ethylene oxide group, PO is a propylene oxide group, n and m are numbers that indicate the average number of the groups in the surfactants, n ranges from about 2 to about 100, and m ranges from about 10 to about 100; polyalkyleneoxide polysiloxanes, optionally polyalkyleneoxide polysiloxane having the general formula:

$$R^{1}$$
— $(CH_{3})_{2}SiO$ — $[(CH_{3})_{2}SiO]_{3}$ — $[(CH_{3})(R^{1})SiO]_{b}$ — $Si(CH_{3})_{2}$ — R^{1}

wherein a + b are from about 1 to about 50, and each R¹ is the same or different and is selected from the group consisting of methyl and a poly(ethyleneoxide/propyleneoxide) copolymer group having the general formula:

with at least one R¹ being a poly(ethyleneoxide/propyleneoxide) copolymer group, and wherein n is 3 or 4, total c for all polyalkyleneoxy side groups has a value of from 1 to about 100, d is from 0 to about 14, c+d has a value of from about 5 to about 150, and each R² is the same or different and is selected from the group consisting of hydrogen, an alkyl having 1 to 4 carbon atoms, and an acetyl group; alkyldiphenyl oxide disulfonate anionic surfactants, having the general formula:

wherein R is an alkyl group; and mixtures thereof.

4. The composition of any of Claims 1-3 wherein said antimicrobial active is selected from the group consisting of: bis-biguanide alkane water soluble salt selected from the group consisting of: chlorides, bromides, sulfates, alkyl sulfonates, phenylsulfonates p-methylphenyl sulfonates, nitrates, acetates, gluconates, and mixtures thereof at a level of from about 0.001% to about 0.4% by weight of the composition, optionally bis-biguanide alkane water soluble salt at a level of from about 0.05% to about 0.2% by weight of the composition that is selected from the group consisting of: chlorhexidine; (1) 1,6-bis-(2-ethylhexylbiguanidohexane)dihydrochloride; 1,6-di-(N₁,N₁'-phenyl-N₁,N₁'-methyldiguanido-N₅,N₅')-hexane tetrahydrochloride; 1,6-di-(N₁,N₁'-phenyl-N₁,N₁'-methyldiguanido-

N₅,N₅')-hexane dihydrochloride; 1,6-di(N₁,N₁'-o-chlorophenyldiguanido-N₅,N₅')hexane dihydrochloride; 1,6-di(N1,N1'-2,6-dichlorophenyldiguanido-N5,N5')hexane $dihydrochloride; 1,6-di[N_1,N_1'-.beta.-(p-methoxyphenyl)\ diguanido-N_5,N_5']-hexane$ dihydrochloride; 1,6-di(N1,N1'-.alpha.-methyl-.beta.-phenyldiguanido-N5,N5')hexane dihydrochloride; 1,6-di(N1,N1'-p-nitrophenyldiguanido-N5,N5')hexane dihydrochloride;.omega.:.omega.'-di-(N1,N1'-phenyldiguanido-N5,N5')-di-n-N₅,N₅')-di-n-propylether tetrahydrochloride, 1,6-di(N₁,N₁'-2,4dichlorophenyldiguanido-N5,N5')hexane tetrahydrochloride; 1,6-di(N1,N1'-pmethylphenyldiguanido- N_5,N_5 ') hexane dihydrochloride; 1,6-di(N_1,N_1 '-2,4,5 $trichlorophenyldiguanido-N_5,N_5') hexane\ tetrahydrochloride;\ 1,6-di[N_1,N_1'-.alpha.-1]$ (p-chlorophenyl) ethyldiguanido-N5,N5'] hexane dihydrochloride;.omega.:.omega.'di(N1, N1'-p-chlorophenyldiguanido-N5,N5')mxylene dihydrochloride; 1,12-di(N₁,N₁'-p-chlorophenyldiguanido-N₅,N₅') dodecane dihydrochloride; 1,10-di(N₁,N₁'-phenyldiguanido-N₅,N₅')-decane tetrahydrochloride; 1,12-di(N1,N1'-phenyldiguanido-N5,N5') dodecane tetrahydrochloride; 1,6-di(N₁,N₁'-o-chlorophenyldiguanido-N₅,N₅') hexane dihydrochloride; 1,6-di(N1,N1'-p-chlorophenyldiguanido-N5,N5')-hexane tetrahydrochloride; ethylene bis (1-tolyl biguanide); ethylene bis (p-tolyl biguanide); ethylene bis(3,5-dimethylphenyl biguanide); ethylene bis(p-tert-amylphenyl biguanide); ethylene bis(nonylphenyl biguanide); ethylene bis (phenyl biguanide); ethylene bis (N-butylphenyl biguanide); ethylene bis (2,5-diethoxyphenyl biguanide); ethylene bis(2,4-dimethylphenyl biguanide); ethylene bis(0-diphenylbiguanide); ethylene bis(mixed amyl naphthyl biguanide); N-butyl ethylene bis(phenylbiguanide); trimethylene bis(o-tolyl biguanide); N-butyl trimethylene bis(phenyl biguanide); and the corresponding pharmaceutically acceptable salts of all of the above such as the acetates; gluconates; hydrochlorides; hydrobromides; citrates; bisulfites; fluorides; polymaleates; N-coconutalkylsarcosinates; phosphites; hypophosphites; perfluorooctanoates; silicates; sorbates; salicylates; maleates; tartrates; fumarates; ethylenediaminetetraacetates; iminodiacetates; cinnamates; thiocyanates; arginates; pyromellitates; tetracarboxybutyrates; benzoates; glutarates; monofluorophosphates; and perfluoropropionates, and mixtures thereof, optionally chlorhexidine.

5. The composition of any of Claims 1-3 wherein said antimicrobial active is present and is quaternary ammonium compound, optionally selected from the group consisting of: benzalkonium chlorides; substituted benzalkonium chlorides; di(C₆-C₁₄)alkyl ammonium salt; N-(3-chloroallyl) hexaminium chloride; benzethonium

chloride; methylbenzethonium chloride; cetylpyridinium chloride; and mixtures thereof, at a level of either from about 0.001% to about 0.8%, or from about 0.001% to about 0.4%, or from about 0.01% to about 0.3%, or from about 0.05% to about 0.2%, by weight of the composition.

- 5. The composition of any of Claims 1-4 additionally comprises at least one of D. L.
- 6. A stable, aqueous food cleaning composition, optionally clear, comprising:
- A. an effective amount to absorb malodors of solubilized, uncomplexed cyclodextrin;
- B. an effective amount to improve the performance of the composition, of cyclodextrin compatible surfactant;
- C. an effective amount, to kill, or reduce the growth of microbes, of cyclodextrin compatible and water soluble antimicrobial active;
- D. optionally, an effective amount of sequestrant/builder to improve cleaning;
- E. optionally, an effective amount to improve acceptance of the composition of hydrophilic perfume containing at least about 50% by weight of the perfume of ingredients having a ClogP of less than about 3.5 and, optionally, a minor amount of perfume ingredients selected from the group consisting of ambrox, bacdanol, benzyl salicylate, butyl anthranilate, cetalox, damascenone, alphadamascone, gamma-dodecalactone, ebanol, herbavert, cis-3-hexenyl salicylate, alphadionone, beta-ionone, alpha-isomethylionone, lilial, methyl nonyl ketone, gamma-undecalactone, undecylenic aldehyde, and mixtures thereof;
- F. optionally, from about 0.01% to about 3% by weight of the composition of low molecular weight polyol;
- G. optionally, from about 0.001% to about 0.3% by weight of the composition of aminocarboxylate chelator;
- H. optionally, an effective amount to reduce foaming, of antifoaming agent;
- I. optionally, an effective amount of metallic salt for improved odor benefit;
- J optionally, an effective amount of enzyme for improved cleaning and odor control benefit;
- K. optionally, an effective amount of solubilized, water-soluble, antimicrobial preservative;

- L. optionally, an effective amount of adjunct odor-controlling ingredients selected from the group consisting of alkali carbonate and bicarbonate salts, low molecular weight water soluble ionic polymers, and mixtures thereof, and
- M. aqueous carrier, wherein the combination of (B). and (C). provides improved antimicrobial activity.
- 7. The composition of any of Claims 1-6 additionally containing at least one of: (1) from about 0.01% to about 3%, by weight of the composition, of low molecular weight polyol selected from the group consisting of: glycerol; ethylene glycol; propylene glycol; diethylene glycol; dipropylene glycol; or mixtures thereof, (2) an effective amount of polyanionic acid or alkali metal salt thereof, having an average molecular weight of less than about 20,000, said polyanionic acid or alkali metal salt thereof optionally being from about 0.001% to about 3% by weight of the composition of said polyacrylic acid or alkali metal salt thereof, having an average molecular weight of less than about 5,000; (3) from about 0.001% to about 0.8% by weight of the composition of quaternary compounds containing two C₁₋₄ alkyl and/or hydroxy alkyl groups and two C₆₋₁₄ alkyl groups; (4), an effective amount of enzyme for improved cleaning and odor control benefit; and (5) from about 1% to about 20% ethanol.
- 8. An article of manufacture comprising the composition of any of Claims 1-7 in a spray dispenser, said spray dispenser optionally comprising a trigger spray device tht is capable of providing droplets with a weight average diameter of from about 10 to about 120 µm.; a pressurized aerosol spray dispenser; or a non-manually operated spray dispenser optionally selected from the group consisting of: powered sprayer, air aspirated sprayer; liquid aspirated sprayer; electrostatic sprayer; and nebulizer sprayer.
- 9. The article of manufacture of Claim 8 wherein said spray dispenser is capable of dispensing said composition as a foam.
- 10. An article of manufacture comprising the composition of any of Claims 1-7 in association with instructions to use it to clean food and/or food contact surfaces by applying it evenly to the surface of said food and/or food contact surfaces and then rinsing said surfaces.

11. The method of cleaning food and/or food preparation surfaces comprising spraying an effective amount of the composition of any of Claims 1-7 onto said surface using either a trigger-spray device optionally forming droplets of the spray have a weight average diameter of from about 10 to about 120 µm., or a pressurized aerosol spray dispenser; or a non-manually operated spray dispenser optionally selected from the group consisting of: powered sprayer; air aspirated sprayer; liquid aspirated sprayer; electrostatic sprayer; and nebulizer sprayer

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C11D3/22 A23F A23P1/00 According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C11D A61L A23P IPC 6 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) C. DOCUMENTS CONSIDERED TO BE RELEVANT Relevant to claim No. Citation of document, with indication, where appropriate, of the relevant passages Category * DE 196 42 600 A (HENKEL ECOLAB & CO OGH) 1,2,6,7 X.P 23 April 1998 3-5,8-11 Α see column 2, line 14 - column 3, line 38 1,6 X DATABASE WPI Section Ch. Week 9228 Derwent Publications Ltd., London, GB; Class D13, AN 92-231257 XP002080770 -& JP 04 156851 A (TOYO INK MFG CO) , 29 May 1992 see abstract 1-11 WO 97 01288 A (PROCTER & GAMBLE) Α 16 January 1997 see page 3, line 15 - page 4, line 11 Patent family members are listed in annex. Further documents are listed in the continuation of box C. Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to filing date involve an inventive step when the document is taken alone "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document of particular relevance; the claimed invention cannot be considered to involve an invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of mailing of the international search report Date of the actual completion of theinternational search 02/11/1998 14 October 1998 Authorized officer Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016 Herrmann, J

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